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Date: October 26, 2004

Janet Szot
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NOV 03 2004
TC 1700

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

US PATENT APPLICATION PUBLICATION: 2004/0166316A1

PUBLICATION DATE: August 26, 2004

SERIAL NUMBER: 10/717,926

FILING DATE: November 21, 2003

APPLICANT: Tamio Noguchi

APPLICANT ATTY. DOCKET: Merck-2801

TITLE: Iridescent Pigment having High Brilliance and High Chroma

Commissioner of Patents
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Dear Sir:

THIRD PARTY SUBMISSION UNDER 37 CFR §1.99

The undersigned hereby files a third party submission in the above-identified US patent application published on August 26, 2004. This submission is filed within two months of said publication. According to the www.uspto.gov's PAIRS, a notice of allowance has not been mailed in the above-identified US patent application publication.

Please charge the \$180.00 fee set forth in 37 CFR §1.17(p) to Deposit Account 05-1070.

A list of the enclosed ten publications including the publication date follows:

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STANDARD PRACTICE
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US Patent 3,087,828 published April 30, 1963;
US Patent 4,086,100 published April 25, 1978;
US Patent 4,744,832 published May 17, 1988;
US Patent 4,867,794 published September 19, 1989;
Mearl **FLAMENCO**® twilight gold pigment product brochure published 3/92;
Mearl **CLOISONNE**® regal gold pigment product brochure published 5/92;
US Patent 5,223,034 published June 29, 1993;
WO 99/20695 published April 29, 1999 (English language counterpart is US Patent 6,596,070.);

Gerhard Pfaff et al., "Angle-Dependent Optical Effects Deriving from Submicron Structures of Films and Pigments", Chem. Rev. 99, pages 1963-1981, published 6/11/99;
and

US 2002/0104461A1 published August 8, 2002.

This submission is also being served under 37 CFR § 1.248 on Applicant at its correspondence address: Csaba Henter, Millen, White, Zelano, and Branigan, 2200 Clarendon Boulevard, Suite 1400, Arlington, Virginia 22201.

Respectfully submitted,



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Ten Enclosures

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3,087,828

NACREOUS PIGMENT COMPOSITIONS

Howard R. Linton, Scotch Plains, N.J., assignor to E. I. du Pont de Nemours and Company, Wilmington, Del., a corporation of Delaware
No Drawing. Filed June 28, 1961, Ser. No. 120,157
15 Claims. (Cl. 106—291)

This invention relates to new pigment compositions.

There are many types of pigments recognized in the prior art. Among such pigments, attention may be drawn to the opaque, high hiding power pigments typified, for instance, by titanium dioxide as a white pigment and by the various iron oxides as colored pigments. It is well recognized that the particle size of such pigments has a profound effect upon their value as pigments, as exhibited in the appearance of compositions in which these pigments are dispersed. Such pigments are generally composed of small irregular particles which behave as small spheres in their interaction with light. To achieve the optimum of opacity and hiding power, the particle size of such pigments is controlled to result in the maximum scattering of the incident light by coating compositions containing these pigments. It has been shown by both theoretical calculations and by practical tests that the light-scattering function increases as the diameter of the particle increases from about 0.1 micron to about 0.2 micron. At 0.2–0.3 micron, there is usually a maximum scattering and then, as the particle size increases further, a rather abrupt drop in scattering power.

Thus, the optical units of prior art high hiding colored and white pigments are generally particles of irregular shape, in the order of 0.2 to 0.3 micron in diameter, which refract and scatter light in substantially the same manner as spheres of very small size. A light beam which falls upon a surface pigmented with such optical units is refracted by each particle it encounters in a completely random manner, and the light is ultimately, in effect, reflected from the film in a random scattering. In the case of colored pigments, some of the wave lengths of light are absorbed so that the reflected light is composed of the remaining wave lengths of light and is thereby colored. In the prior art manufacture of such pigments, it has been a principal aim to maximize the random light scattering by control of particle size and shape.

Another class of pigments widely used in the prior art may be designated under the general term "flake pigments." In one of the oldest uses of such pigments, the flakes are used as reinforcing and protective pigments wherein the flake-like particles are oriented in a leafing or overlapping fashion, more or less parallel to the surface of the paint or other film, and thus create a physical barrier to the penetration of the film by deleterious agents as well as providing a reinforcing effect. Water-ground white mica in small sizes (200–325 mesh) has been widely used for this purpose. It is substantially colorless, and its refractive index (about 1.55) is essentially the same as that of the common paint vehicles; thus, it has a negligible effect on the visual properties of the film. However, when used in low refractive index vehicles or when partially exposed to the air, mica has a reflective and sparkling effect and has, on some occasions, been used for this effect.

Atwood, in U.S. Patent 2,278,970, has combined the reinforcing effect of mica with the high hiding power properties of other pigments, such as titanium dioxide, to give a composite pigment which is said to be an intimate association of mica with another pigment, exhibiting the general properties of the second pigment, but without the sparkling effect of the mica. In order to hide the sparkle of the mica and to obtain the general appearance

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of the second pigment, the particle size of this second pigment must be such as to result in a maximum, or a near-maximum scattering of light. In the case of titanium dioxide, particles in the range of 0.2–0.3 micron in diameter are necessary to achieve this result.

Other types of flake pigments include metal flakes, especially aluminum in various particle sizes, which have been used both for the purpose of reinforcing effects and for the essentially opaque character and shiny surfaces of such flakes, giving a film with the appearance of a metal surface.

Metal flake pigments, such as aluminum, have also found wide use because of their decorative effect, especially when mixed with other pigments, to give the well known "metallized" appearance of many automotive finishes. Despite their desirable appearance, such metallized finishes have certain well recognized defects, including a tendency to water spot, which is a persistent discoloration of the finish when water is allowed to stand on it in drops, especially when the water is slightly alkaline as from a detergent. It is also common to find that a mixture of aluminum flakes with a colored pigment is less lightfast than the colored pigment alone.

A third and more specialized use of certain flake pigments is to create finishes with a nacreous or pearl-like effect simulating the appearance of mother of pearl with its three dimensional effect of luster in the depth of the film. Pigments having this effect are non-opaque with a high refractive index and vary in nature from an extract of fish scales, essentially the organic compound guanine, to flake-like crystals of certain inorganic salts, notably basic lead carbonate and lead acid phosphate. In spite of their valuable decorative properties, these products have well recognized deficiencies such as:

(1) They cannot, in general, be handled in dry form but must be stored and marketed as dispersions in the selected vehicles in which they will be used.

(2) Their lightfastness does not meet the demands of many outdoor uses.

(3) They are inherently very expensive to manufacture.

(4) The presence of lead compounds is frowned upon in many potential uses.

This invention provides a new group of nacreous flake pigments which can be marketed in a dry, easily dispersible form, which have excellent lightfastness, are generally non-toxic in character and relatively low in cost. They are capable of being formulated to give very desirable nacreous effects and, moreover, within the broad group, there are many products with pronounced color in addition to their nacreous character, the color being derived, at least in part, from the optical phenomenon of interference. Furthermore, these products may also be formulated to simulate a metallized appearance completely free from the water spotting so characteristic of finishes based on aluminum flakes. Finally, since they are flake-like in nature and chemically stable, they have the added ability to serve as reinforcing pigments.

All pigments exhibiting nacreous effects when dispersed in vehicles have certain common optical and physical characteristics which set them apart from the usual colored pigments and white pigments of commerce. In contrast to the irregularly shaped pigment particles described above, which behave optically much like small spheres, nacreous pigments are non-opaque flake-like products in which the optical units are extremely thin flakes, at least about 5 to 10 microns in major diameter and in the range of about 0.1 to 3 microns in thickness. Such optical units minimize the scattering of light and result in direct reflectance or sparkle.

Furthermore, all nacreous pigments must be transparent or translucent in character, and they must exhibit

a substantial difference in refractive index from the medium in which they are dispersed. Thus, the common coating composition vehicles, plastics, and the like have refractive indices generally in the range of about 1.5 to 1.6. Those pigments which have been known in the prior art as nacreous pigments have, in general, refractive indices in the range of about 1.8 to 2.6. Most prior art nacreous pigments are thin flakes of a definite chemical compound. These thin flakes, in the presence of a vehicle of low refractive index, exhibit the optical behavior of thin films including light interference and a resultant interference color characteristic of the thickness of the film. However, the prior art flakes exhibit more or less random thicknesses, and the average effect is a blending of colors to give a nacreous or pearl-like appearance almost free of distinguishable color.

The optical principles which explain interference colors are well known and are discussed in many textbooks of physical optics such as Robert W. Wood, "Physical Optics, 3rd edition," New York, 1936, page 198. Briefly stated, interference is an optical phenomenon associated with the reflectance of light from the surfaces of thin films, wherein there is a reduction in the intensity of certain wave lengths of the incident light (destructive interference) and reinforcement of other wave lengths (constructive interference). The extent to which particular wave lengths are affected is dependent upon the thickness of the film and its refractive index. When the thickness is such that a ray reflected from one surface of a film is out of phase with a ray which has passed through the film and been reflected from the other surface, there is destructive interference.

Since there is a phase reversal when light is reflected from the surface of a medium of higher refractive index, the condition of maximum destructive interference (minimum reflectance) is satisfied when the effective optical path (thickness multiplied by refractive index) in a film of high refractive index in one wave length or a simple multiple thereof. Considering the refractive index, "N," of the film, the thickness (*t*) thereof for destructive interference with any wave length "*λ*" is given by the formula

$$t = \frac{n\lambda}{2N}$$

where "*n*" is a small whole number usually not greater than 5.

By the same line of reasoning, if the two rays emerge in phase, there is reinforcement or a maximum of reflectance. This condition is satisfied, again assuming phase reversal, when the effective optical path is one half a wave length or an odd multiple thereof, the formula for the thickness at maximum reflectance being

$$t = (n + \frac{1}{2}) \frac{\lambda}{2N}$$

where "*n*" is 0 or a small whole number usually not greater than about 5.

When "*n*" is greater than 1, it is common to speak of the interference as a higher order, second order, third order, and the like. For thick films, there are interference bands at various wave lengths in the visible spectrum and the resultant colors are generally low in intensity.

It is now found that a thin, adherent, translucent layer of a colorless titanium or zirconium oxide of a selected small particle size can be deposited in a preferred oriented arrangement on the smooth surface of a translucent flake pigment, such as mica, to give a hitherto unknown family of slightly colored nacreous flake pigments which are relatively free from random scattering of light and which derive their color solely from the optical phenomenon of interference. It is further found that an additional adherent, translucent layer of a second metal oxide which may in itself be colored, can be deposited on, or intermingled with, the titanium oxide (or zirconium oxide)

coated mica to give new products with an enhancement of color and improvements in other properties. When dispersed in a conventional manner as pigments in various systems, the compositions so obtained exhibit novel color effects, including a brilliant nacreous luster and, especially when viewed at the specular angle under bright illumination, as in the sunlight, they exhibit a striking iridescent sparkle on a background of a predominating color. When the oxide coatings are all inherently colorless, the observed color is solely the result of optical interference and varies in hue from a silver pearl through gold and red to blue and green as the thickness of the combined oxide layers increases. When a colored oxide is coated onto a titanium or zirconium oxide layer, both the inherent color of the second oxide and the interference color of the combined layers may be observed as a variety of spectacular effects.

The new nacreous flake pigments of this invention comprise two parts—(1) a non-opaque flake substrate, and (2) a thin, adherent, translucent layer of metal oxide of selected small particle size deposited thereon which metal oxide layer must include a layer of titanium oxide or zirconium oxide and may include a second oxide, either as a separate layer or in admixture with the titanium or zirconium oxide.

In a preferred embodiment of this invention, the non-opaque flake substrate is a flake-like micaceous mineral, usually muscovite mica, in a selected particle size range. Such flake substrates useful for the purposes of this invention are particles which have two dimensions (length and width) of similar magnitude and characteristically much greater than the third dimension. Specifically, the preferred flakes of this invention are at least about 5 to 10 microns in a major dimension and in the range of about 0.05 to 1.0 micron in thickness. For most pigment purposes, the upper limit in the major dimension is from 50 to 100 microns. However, for specialized uses such as in plastic articles of appreciable thickness, linoleum, and the like, larger flakes up to as much as 1 mm. length may be used for special decorative effects. The lower limit in thickness of the mica flake is determined to a large extent by the physical strength of the flake and may be as little as 0.05 micron or even less, while an upper limit of about 3.0 microns, accompanied by a correspondingly greater length and width, is fixed by the effect on the coating composition surfaces. Such flakes must also be substantially planar with a relatively smooth and light reflecting surface and must be insoluble in either water or organic solvents and inert thereto.

A satisfactory grade of mica is a water ground white mica, frequently used as a reinforcing extender pigment in paint, all of which passes through a 200 mesh screen and about 90% through a 325 mesh screen. A mica pigment meeting ASTM specification D-607-42 is a preferred grade. However, for specialized purposes, it is quite possible to use flakes which are in the 140 mesh to 200 mesh range on the one hand as well as material which is considerably finer, approaching the 400 mesh size or even finer.

Another measure of particle size, more readily correlated in many ways with the application of the subsequent metal oxide film to the surface, is the specific surface area as measured by gas adsorption using the well-known BET method. This function has been found to vary appreciably from batch to batch of nominally similar sized micas. Mica with a surface area of about 3 square meters per gram and with a reasonably uniform particle size is a particularly suitable form. However, products of acceptable properties may be obtained from samples of mica with widely differing surface areas provided appropriate adjustments are made in the amount of metal oxide applied to form the transparent layers thereon so that the use of metal oxide per unit of surface area is appropriately controlled. No arbitrary limits on surface area can be established, but a range from about 2 sq. meters

per gram to about 7 sq. meters per gram will encompass the products most likely to be desired.

In addition to the preferred muscovite or white mica, other forms of mica such as biotite, phlogopite, related vermiculite, and various synthetic micas, especially those which resemble natural white mica, may be used as substrates in this invention. To obtain these products in the desired particle size ranges, it is preferred that they, also, be water ground. The introduction of agents to facilitate exfoliation or the introduction of other inert coatings which do not materially alter the refractive index of the mica nor its receptivity to the subsequently applied translucent layer of titanium oxide are contemplated as being within the scope of this invention. The inherent color of some of these micas influences the color of the final products, but the interference colors of the films deposited will still be present.

The preferred material for the thin translucent layer of metal oxide deposited upon the mica substrate is an oxide of tetravalent titanium, such as TiO_2 , the particles of which are less than about 0.1 micron in diameter. Such a layer of TiO_2 , as the hydrous oxide, is conveniently deposited upon a mica substrate by suspending the mica in a dilute, strongly acidic solution of titanyl sulfate at ambient temperature and then hydrolyzing the titanium sulfate solution by rapidly heating to about 90–100° C. and maintaining at that temperature for about 2–3 hours so that the hydrous titanium dioxide as formed is continuously deposited on the mica with a minimum of formation of free hydrous titanium dioxide. Alternately, the mica may be suspended in hot water to which is then rapidly added a strongly acidic concentrated titanyl sulfate solution, after which hydrolysis and deposition of the hydrous titanium dioxide on the mica are brought about by continued heating at the boil until hydrolysis is complete. The choice between these methods is a matter of convenience.

Upon isolation of the resulting pigments by filtration and drying, there are obtained nacreous powders exhibiting brilliant interference colors when dispersed in a vehicle, the predominating color depending (at least in part) upon the thickness of the hydrous oxide film.

The color of the products obtained in this manner is rather subtle and is most readily observed when a film containing these new nacreous pigments is observed over a dark background. In addition to the predominant interference color, substantially all of these products show a brilliant iridescence or a multicolored sparkle when observed at the specular angle under bright illumination, as in the sunshine. This combination of iridescence on a background of a predominating color is an outstanding characteristic of the new products.

The new products containing hydrous TiO_2 on mica, as directly prepared by the hydrolysis of a titanyl sulfate solution in the presence of mica, although very beautiful in color effects and useful for some purposes where not generally exposed to light, are quite photosensitive, showing marked changes in pigmented compositions containing them on exposure to light. Consequently, they require stabilization in this property for their most effective uses. This photosensitivity is believed to derive in part from either one of two causes. On the one hand, dry hydrous TiO_2 invariably contains an appreciable amount of acidic impurities which cannot be removed by the usual techniques of isolation of the pigment. Partial stabilization to sensitivity from this cause can be brought about by the deposition of certain other metal oxides, particularly hydrous alumina or hydrous chromic oxide, upon the layer before final drying. More effective stabilization is, however, brought about by calcination at temperatures in the range of 700–1000° C., preferably in the 900–1000° C. range. Products obtained by calcination in these temperature ranges retain their brilliant interference colors to a large extent, although the predominant colors shift slightly in the direction which indicates a reduction in the thickness

of the layer of oxide, as would be expected by the driving out of certain impurities, including water and residual acid.

It is well known in the art that certain impurities have a profound effect on light sensitivity of titanium dioxide. This effect is also found in the pigments of this invention. For instance, very small amounts of iron which may be introduced through the use of impure raw materials or by migration from the mica during calcination are found to cause light sensitivity to increase. On the other hand, certain impurities may be deliberately introduced by the proper selection of raw materials or the addition of appropriate salts to the titanyl sulfate solution to bring about remarkable improvements in reducing photosensitivity. Compounds of antimony, niobium, chromium, tungsten, molybdenum, and even iron when used in substantial amounts, serve in this way. An especially valuable procedure is to add small amounts of an antimony compound, for instance, antimony oxide (in the range of 0.5 to 5%, preferably about 2%, based on titanium dioxide present) prior to the calcination. In any case, small amounts of a second metal oxide, not exceeding about 20% by weight of the titanium oxide, may be included in the titanium oxide layer, either as an impurity or by deliberate coprecipitation.

An alternative procedure for depositing the film of titanium dioxide involves the exposure of hot ($\pm 600^\circ$ C.) flakes of mica to the vapor of an organic titanate ester such as tetraisopropyl titanate in the absence of air or water vapor, and preferably in a vacuum. Likewise, other water-soluble salts of titanium may be used in the hydrolysis procedure. Thus, in particular, titanium oxychloride can be used on the one hand, as can certain water-soluble titanium esters such as titanium acetyl acetate and triethanolamine titanate on the other hand.

Furthermore, a zirconium dioxide coating can be used in place of the titanium dioxide coating. It may be applied in a similar manner, and in similar amounts, by the hydrolysis of a solution of a suitable zirconium salt (zirconium oxychloride or zirconium sulfate, for instance) in the presence of mica. It is a peculiarity of anhydrous zirconium oxide that it has a significantly lower refractive index than hydrous titanium oxide so that the products containing the simple layers of hydrous zirconium oxide are appreciably less nacreous in character than products containing titanium oxide. However, upon calcination, a pronounced nacreous character is developed.

It is also contemplated that a second layer of metal oxides may be deposited on top of, or intermingled with, the titanium oxide or zirconium oxide layer. This second layer may consist of colorless oxides such as alumina, zirconium oxide, zinc oxide, tin oxide, antimony oxide and the like, or even a second layer of titanium oxide. On the other hand, it may include oxides which have inherent color such as iron oxide, nickel oxide, cobalt oxide, copper oxide, or chromium oxide. This second layer of oxide obviously alters the thickness of the total oxide layer, and thus contributes to the interference phenomenon. It may also contribute inherent color of its own, together with the interference color, giving largely unpredictable tinctorial effects of great interest.

The titanyl sulfate solution used in the preferred processes may be obtained in any convenient manner. Thus, a relatively pure titanyl sulfate may be obtained by dissolving in sulfuric acid a hydrous titanium oxide precipitate commonly obtained as an intermediate in the preparation of TiO_2 pigment. However, it has been found that such highly pure solutions are not necessary and that equivalent results can be obtained by using a conventional titanyl sulfate concentrate prepared from the ore and containing a small amount of iron which is maintained in the divalent state by the presence of a small amount of trivalent titanium in the strongly acid solution. Thus, the concentration of the titanyl sulfate in the

aqueous solution may vary over a range, say, preferably from about 2 parts (calculated as TiO_2) to about 20 parts per 100 parts of solution. Regardless of the concentration, it is necessary that there be free acid in the solution at all times over and above that necessary to convert all of the titanium oxide to TiOSO_4 . This is necessary to prevent precipitation of a hydrous titanium oxide at room temperature. The titanium oxide art conventionally uses a "factor of acidity" (F.A.) as a parameter to define this relation where,

$$\text{F.A.} = \frac{100 (\text{total acid} - \text{combined acid})}{\text{Combined acid } (\text{TiOSO}_4)}$$

In the examples below, F.A. values of about 80 for a concentrated titanyl sulfate solution and about 220 for a more dilute titanyl sulfate are shown. Values in the range of about 50 to 300 are preferred for the best results. The critical condition is that there be sufficient acid to prevent hydrolysis at room temperature but not sufficient to repress hydrolysis excessively at elevated temperatures. The desired conditions will obviously vary somewhat with concentrations of reactants and with temperature and, within within a broad range, the conditions may be readily determined by the skilled worker. In general, the preferred F.A. values are within the range considered optimum for the preparation of pigment-grade TiO_2 .

Regardless of the source of the titanyl sulfate and regardless of the concentration in the starting material, the concentration of the titanium salt in the solution in which the mica is suspended at the point of hydrolysis is more dilute by a factor of at least 2 or 3 than is preferred for TiO_2 pigment. For the best results in this invention, this concentration of titanium salt (calculated as TiO_2) in the solution at the point of precipitation should be at least about 2 parts and should not exceed about 7 parts per 100 parts of solution.

The amount of the titanium (or zirconium) salt used in relation to the mica may vary over a wide range and is significant only as a control on the thickness of the ultimate oxide coating. In general, the usage, calculated as TiO_2 (or ZrO_2), should be in the range of about 10 parts per 100 parts of mica (about 10%) up to as much as about 200 parts per 100 parts of mica (about 66%) with a preferred range for TiO_2 of about 15 to 80 parts per 100 parts of mica (about 15-40% of TiO_2). This is, of course, reflected in the thickness of the layer deposited and the resulting interference color. It has been found that when the amount of TiO_2 is in the range of 10-26% by weight of the product, a silver-colored pigment is usually obtained; in the range of 26-40%, the pigment is golden in color; and in the range of 40-50%, the color of the pigment varies from red to blue to green as the thickness of the metal oxide layer is increased. In the range of 50-50%, higher order interference colors are obtained. Other means have also been used in this invention to correlate thickness of film with interference color. For example, a convenient measure of the thickness of the layer is the weight of TiO_2 deposited per unit area of mica surface (conveniently expressed as milligrams per square meter of mica surface) and this may vary from about 50 mg. of TiO_2 to 600 mg. of TiO_2 or more per square meter of surface. In the upper portions of this range, the observed colors are higher order interference colors. The relation between the weight of TiO_2 per square meter and the color varies somewhat between uncalcined and calcined products. However, within broad limits, the following table sets forth the correlation between the observed interference colors and the measured TiO_2 weight per square meter of mica surface. Since color hues vary continuously over the spectrum, it is obvious that the ranges merge at the dividing points. Pigments having 50-280 milligrams of TiO_2 per square meter

of mica surface exhibit first order interference colors, and they are preferred materials.

Color:	Mg. TiO_2 per square meter
Silver	50 to 100
Gold	100 to 180
Red	180 to 220
Violet	220 to 240
Blue	240 to 260
Green	260 to 280
2nd order gold	280 to 350

The weight of ZrO_2 per square meter will be somewhat larger than these figures because of the higher density. The general principles, however, apply.

Another means for measurement of the thickness of the TiO_2 layer in relation to the color, which depends upon direct measurement and not upon prior knowledge of the nature of the mica or the TiO_2 coating, is derived from the wave lengths of the interference bands using the formulas given above in the discussion of interference. The wave lengths of the interference bands can be readily determined from spectrophotometric curves made in the conventional manner on dispersion of the colors over black backgrounds. From these measurements of wave length, optical paths can be calculated ($\frac{1}{2}$ of the wave length of the first order minimum or $\frac{1}{4}$ of the wave length of first maximum), and it follows that the optical path divided by the refractive index gives a calculated thickness which varies with the color as defined in the spectrophotometric curves. It is well known that the refractive index of TiO_2 varies with the wave length (see Schroeder-Zeit. für Kristallographie 67, 485-542 (1928)), and, in the table which follows, allowance for this variation has been made in calculating the thickness. Since the coatings are known to be particulate (based on electron micrographs) and contain voids, the correlation between this calculated thickness and a calculated thickness based on the known weight of TiO_2 per unit area and the specific gravity of the TiO_2 must make allowance for these voids as well as for some possible unevenness of coating on all of the surfaces of the mica measured by the BET method. Making reasonable allowances for these factors, the correlation is excellent.

In the following table, the optical path has been calculated from measurements of interference bands exhibited by typical products of known composition. Where possible, interference bands, either maxima or minima, falling in the visible portion of the spectrum have been used for the calculation. The silver flakes, however, have no interference bands in the visible spectrum and there is considerable uncertainty about the exact position of the interference band in the ultraviolet because of an absorption band of TiO_2 in the same region. Measurements of thickness are in millimicrons. Weight of TiO_2 per square meter is in milligrams, and they are based on direct measurements.

Color	Optical path (in millimicrons)	Geometric thickness (in millimicrons)	TiO_2 per square meter (in milligrams)
Silver	196	135	85
Pale gold	150	59	145
Gold	175	71	163
Red	250	95	186
Violet	297	117	231
Blue	325	129	250
Green	358	145	275
2nd order gold	412	161	320
2nd order violet	457	194	385

¹ Estimated.

From these illustrative data, it is apparent that products of technical merit are found throughout a range of about 30 to 200 millimicrons in the calculated geometric thickness of the oxide layer. It has been found in other studies that a broader range of about 20 millimicrons to about

250 millimicrons is also useful with the range of about 20-155 millimicrons for the first order interference colors as preferred.

The following table gives the color obtained within various ranges of thickness.

Color:	Geometric thickness range (in millimicrons)
Silver	20-40
Pale gold, gold	40-90
Red	90-110
Violet	110-120
Blue	120-135
Green	135-155
2nd order gold	155-175
2nd order violet	175-200

The thickness of a ZrO_2 layer may vary to a small degree from the figures given above, since ZrO_2 has a slightly lower refractive index.

The isolation of the pigments of this invention by filtering, washing, and drying is entirely conventional. However, it is well known that a certain amount of sulfate ion is very tenaciously held by a hydrous titanium dioxide precipitate, and it is sometimes desirable to favor the more complete removal of this sulfate by washing with a dilute alkaline solution such as dilute ammonium hydroxide, either on the funnel or by reslurrying in such a solution, followed by filtering and washing again.

It appears that one of the critical features distinguishing the new products from the titanium dioxide pigments of the prior art lies in the character of the titanium oxide deposited on the mica flakes. Examination of such flakes, both before and after calcination, in the electron microscope, suggests that the hydrous oxide film has particles so small as to be very poorly resolved in the electron microscope. They are not completely non-crystalline because they have a distinguishable X-ray diffraction pattern and there is some evidence of very small, in the order of 0.01 micron in size, particles, but these particles do not appear to have sharp edges and tend to be irregular in size and shape. Upon calcination, a definite crystalline pattern becomes evident but the crystallites are still extremely small and densely packed so that the optical character is that of a film. Measurement of these particles shows a maximum particle size of about 0.1 micron for any calcination temperature below about 1000° C. In the preferred calcination temperature range of from about 700 to about 1000° C., substantially all of the particles are appreciably less than 0.1 micron in diameter. At higher temperatures, some larger particles do appear and when the particles of TiO_2 , or other oxide, substantially exceed 0.1 micron in diameter, the interference colors and the nacreous character of the product are no longer apparent. Such products exhibit the light-scattering properties of conventional TiO_2 or other pigments.

In the deposition of a second metal oxide layer, it may be deposited upon either a hydrous titanium or zirconium oxide layer or upon the corresponding calcined layer or it may be deposited simultaneously with the titanium oxide layer by adding an appropriate metal salt to the titanyl sulfate solution. In general, the second oxide is deposited in a lesser amount than either the titanium or zirconium oxide. One of the most outstanding results from the deposition of such a second metal oxide is a marked stabilization of the photosensitivity of the initial hydrous TiO_2 layer. Alumina hydrate lends itself admirably for this purpose. This material has a relatively low refractive index, and it produces stabilization with a relatively minor effect on the color of the interference. It is most effectively deposited as a second layer by thermal hydrolysis from a buffered solution such as aluminum acetate.

Other oxides which may be deposited include the following:

(1) Zinc oxide (ZnO) may be deposited by thermal

hydrolysis of an ammoniacal zinc complex solution such as tetrammine zinc sulfate. When such a combined layer of hydrous TiO_2 and ZnO is calcined, the resulting layer exhibits the X-ray pattern of rutile TiO_2 whereas the single layers of TiO_2 show anatase TiO_2 . In general, this variation appears to have a minor effect on the properties of the coated flakes.

(2) Zirconium oxide (ZrO_2) may be deposited as the hydrous oxide on top of hydrous TiO_2 by the thermal hydrolysis of a solution zirconium oxychloride, for instance. It improves the stability to light with a minor effect on color. On calcination of the combined layers, however, there is an increase in refractive index which results in a color effect to be anticipated from a thicker film.

(3) An iron oxide layer (Fe_2O_3) may be deposited by the thermal hydrolysis of a solution of ferric acetate, for instance. The resulting product, prior to calcination, is a brilliant gold flake pigment of pronounced color which varies with the thickness of the combined layers and is accompanied by an iridescent sparkle. Such pigments impart a pronounced two-tone effect to compositions containing them. On calcination, there is a color change toward the red, in line with the known behavior of iron oxides, retaining to a large extent, however, the nacreous effect.

(4) Nickel oxide is readily deposited on a hydrous TiO_2 -coated mica by the thermal hydrolysis of a nickel tetrammine sulfate solution, for instance. The color effects in this case after calcination, as shown in Example XV are quite unexpected.

Nickel oxide may also be deposited by thermal hydrolysis of a nickel acetate solution.

(5) Cobalt oxide is readily deposited by the thermal hydrolysis of a cobalt acetate solution.

(6) Some of the most unexpected effects are obtained with chromium oxide (Cr_2O_3). It is deposited readily by the thermal hydrolysis resulting from the volatilization of ammonia from a solution in water of hexammine chromium (III) derivative or by the thermal hydrolysis of a chromium salt solution, buffered with borax. A very thin layer (1% to 2% of Cr_2O_3 based on the TiO_2) deposited on a hydrous TiO_2 layer has resulted in marked stabilization of the photosensitivity with very little effect on the color of the pigment. Moreover, this thin layer of chromium oxide seems to stabilize the color on calcination so that such products are improved both in color and in stability to light over untreated products.

If, on the other hand, a large amount of Cr_2O_3 (5-15% based on the TiO_2) is deposited, for instance, on top of a hydrous TiO_2 with a gold interference color and the resulting flake pigment calcined, the final product is an attractive golden nacreous pigment with an iridescent sparkle which imparts an interesting two-tone effect to compositions pigmented therewith.

It is obvious that other metal oxides not specifically mentioned, can be incorporated into these flake pigments in like manner.

The above illustration with chromium oxide points to the importance of variations in the thickness of the successive layers in multilayer coatings. The amount of titanium oxide or zirconium oxide in the initial layer may vary over the whole range shown for the single layer. The resulting colors will significantly affect the properties of the final products. In like manner, the second layer may be varied in thickness by controlling the amount of reagent used and the conditions of deposition. The thickness of the second layer contributes to the interference color in the expected manner, subject to variations in the refractive indices. The invention contemplates ranges in the individual layers of the multilayer coating comparable to those shown for TiO_2 alone.

It is quite apparent that the deposition of successive layers of metal oxides can be extended beyond two successive layers and the invention should be understood as

contemplating such multilayer coatings. It is also contemplated that thick layers of titanium oxide may be deposited in a single step or may be deposited in successive steps with or without a calcination step between.

In discussing the properties of these new pigments, emphasis has been placed on compositions in which they are used alone. It has been pointed out, however, that the color is most readily observed over dark backgrounds. It is also possible to develop similar effects by mixtures with other pigments. Thus, mixtures with carbon black can be formulated to give effects very similar to those obtained by lamination over a black surface. In mixtures with colored pigments, the nacreous character, and frequently the sparkle as well, are retained while the effect on the color is often far greater than might be anticipated from the relatively subtle color of many of the flakes alone. Many combinations have an effect not unlike that of aluminum flakes except that the proportions of the new flakes to the color can be much higher than when aluminum flakes are used since the new flakes are more transparent than the metal flakes.

When the new flakes are used in admixtures with conventional pigments of high hiding power, such as pigmentary TiO_2 for instance a pronounced nacreous, or pearl-like, character is quite evident even with as much as 25 to 50% of TiO_2 , but the iridescent sparkle may be very much diminished. Nevertheless, such mixtures offer attractive possibilities to the formulator.

An outstanding property of the new flake pigments is their remarkable ease of dispersibility in coating composition vehicles. It has been considered necessary with substantially all pigments known to the art to subject them to considerable grinding action for the necessary degree of dispersion required in formulating high quality paints, enamels, and the like. TiO_2 requires substantial grinding to give acceptable enamels. Mica also requires considerable work on the system for good dispersion. It is, therefore, totally unexpected to find that the new pigments, whether calcined or not, can be dispersed in a great variety of vehicles by simple vigorous agitation. Additional grinding shows little, if any, advantage and can be easily carried to the point where the flakes are broken with an undesirable effect on the color obtained.

Although these new pigments are spoken of as exhibiting interference colors of specified hues in the examples which follow, these colors are often very subtle and are best observed under certain specific conditions. Thus, many of the powders in bulk show little color, being almost white or slightly yellowish. If the powder is spread in a thin film such as by rubbing between the fingers, and observed in a bright light, it shows a pronounced sparkle and definite color. If it is mixed with water on a black surface, the color and sparkle immediately become visible.

Such pigments have their principal value as ingredients of compositions such as paints, printing inks, plastic films, rubber articles, and the like to which they impart color and other decorative effects and often exert a profound influence on the durability of such compositions on exposure to the elements. When the color and decorative properties of pigments are spoken of, it is generally understood that reference is being made to compositions containing the pigments of which the following are typical, but not limiting.

FORMULATION A.—UNSUPPORTED FILM OF CELLULOSE ACETATE

1.0 part of pigment is added to 20 parts of a cellulose acetate solution containing 16.7% cellulose acetate in acetone. The mixture is stirred until thoroughly mixed. A glass plate is prepared for stripping a film therefrom by coating the clean plate with a silicone stopcock grease and then wiping thoroughly with a dry cloth. The lacquer is spread on the glass plate and drawn down to a wet film thickness of about 0.16 mm. After the solvent has evaporated,

the film is stripped from the plate and observed on the smooth side. Such films are conveniently used for light-fastness tests in a "Fade-Ometer."

FORMULATION B.—BAKED ACRYLIC LACQUER

	Parts
Pigment	2.5
Mixed acrylic ester polymer ("Acryloid" A-101, Rohm and Haas)	17.9
Butyl benzyl phthalate	7.7
Mono-acetate of ethylene glycol monoethyl ether ..	20.0
Methyl ethyl ketone	56.9
Toluene	50.0

The pigment is dispersed by vigorous stirring with the resin and plasticizer together with a portion of the solvents for about 15 minutes; the remainder of the solvents is then added and the mixing continued until uniform. Exhibits are prepared by spraying onto primed panels and, after drying, baking at 80–85° C. for 20 minutes. Alternatively, as a quick testing method, films of this lacquer may be spread to uniform thickness with a "doctor blade" and observed after air drying.

FORMULATION C.—BAKED ALKYD ENAMEL

	Parts
Pigment	2.5
Non-oxidizing coconut oil-modified alkyd resin solution (60% solids)	29.2
Modified melamine formaldehyde resin (55% solids)	13.6
Aromatic hydrocarbon solvent	15.0
Aliphatic hydrocarbon solvent	19.0

The pigment is added to the mixed resin solutions with a part of the solvent and dispersed by high speed stirring for about 15 minutes after which the remainder of the solvent is stirred in. The resulting enamel is sprayed onto a primed metal panel and baked one half hour at about 120° C. Films of uniform thickness may also be applied with a "doctor blade."

FORMULATION D.—VINYL PLASTIC FILM

	Parts
Pigment	3
Vinyl chloride polymer	100
Dioctyl phthalate	40
Polyester resin	10
Stabilizer (barium-cadmium-zinc phosphite)	3
Stearic acid	0.25

The pigment is added to the mixture of ingredients and the whole mixture is processed on a two roll mill, heated to 155° C., until uniform. It is finally taken from the mill as a sheet of any desired thickness which may be observed as obtained or may be press polished in a suitable heated press.

These compositions are all conventional and may be modified in well-known ways or may be replaced by equally conventional compositions including cellulose nitrate lacquers, linseed or other oleo resinous varnishes, linoleum compositions, rubber, polyethylene resins and the like.

In all cases, as previously pointed out, the observed color can be confirmed by optical measurements such as spectrophotometric reflectance curves which can be determined by measurements on dispersions of the colors over black backgrounds.

Such measurements give reflectance curves which conform to the observed color. Where the oxide coating is inherently colorless, there is a progressive shift to longer wave lengths for the reflectance minima as the thickness of the coating increases. For instance, in a series of samples with increasing amounts of TiO_2 in a single coating, the wave lengths of the minimum and maximum re-

reflectance values for typical samples vary with the color as follows:

WAVE LENGTH OF 1st INTERFERENCE BAND		
Color	Minimum	Maximum
Silver.....	In the ultraviolet.....	About 390 millimicrons.
Gold.....	390 millimicrons.....	700 millimicrons.
Red.....	600 millimicrons.....	970 millimicrons.
Violet.....	570 millimicrons.....	1,100 millimicrons.
Blue.....	600 millimicrons.....	1,170 millimicrons.
Green.....	685 millimicrons.....	1,350 millimicrons.

WAVE LENGTH OF 2nd INTERFERENCE BAND		
Gold (2nd order).....	430 millimicrons.....	550 millimicrons.
Violet (2nd order).....	500 millimicrons.....	650 millimicrons.

When a multilayer coating contains an oxide which is inherently colored, the spectrophotometric curve shows both the absorption bands of the inherent color and the interference bands due to the thin film on the translucent flake pigments.

The following examples illustrate but do not limit the invention. In all cases, unless otherwise specified, all parts refer to parts by weight.

Example I

580 parts of an aqueous titanyl sulfate solution containing 4.4% TiO_2 as titanyl sulfate (equiv. to 25 parts TiO_2) and F.A. of 217 is diluted with 500 parts of water. 100 parts of mica is then suspended in this solution. The mica is a water-ground white mica (muscovite) having the trade name "Concord Wet Ground Mica #200/325." This mica has a specific surface area of about 3.3 square meters per gram, as determined by krypton adsorption in the previously mentioned BET Method; it all passes through a 200 mesh screen and about 94% through a 325 mesh screen. The average particle size is in the range of 20-40 microns in maximum dimension and about 0.1 micron in thickness. The suspension of mica in the titanyl sulfate solution is heated rapidly (about 10 minutes) to the boil and maintained at the boil under reflux for about 2½ hours. The product is isolated by filtering and washing with water to a pH of 5.0. After drying at 80° C., there is obtained about 135 parts of a finely divided flake pigment which requires no further particle size reduction. In bulk form, this flake pigment is a shiny, slightly yellow powder. It may be readily dispersed in various coating composition vehicles by simple high-speed stirring. When dispersed in an alkyd resin vehicle as in Formulation C and coated over a black, primed metal surface, the resulting surface has a silvery appearance and a lustrous iridescent sparkle in the sunshine.

Example 1a

This portion of the example illustrates how a change in color can be obtained by using a larger amount of titanyl sulfate solution, thus depositing a thicker layer of hydrous TiO_2 .

If the procedure of Example I is followed except that

the amount of titanyl sulfate solution is increased to 1160 parts (50 parts TiO_2), the yield of flake pigment is about 150 parts of shiny powder with a slightly more yellowish tinge. When dispersed in the alkyd resin vehicle and coated over a black primer, a golden appearance and a pleasing lustrous iridescent sparkle are obtained, especially when viewed in the sunshine.

Example II

The mica used in this example is of a larger particle size than that used in Example I. It was obtained by screening the mica of the previous example and collecting the portion which passes through a 200 mesh screen and is retained on a 325 mesh screen.

100 parts of this -200/+325 mesh mica is slurried in 1160 parts of the titanyl sulfate solution of Example I, and the mixture is treated in the manner described in that example. Because of the larger particle size of the mica, the surface area per gram is less so that the same amount of titanyl sulfate produces a thicker coating on the mica flakes than was obtained in Example 1a. When the flakes are dispersed in a coating composition vehicle and coated over a black surface, a blue appearance and a pleasing lustrous sparkle are obtained.

By using the above conditions and a still larger mica flake which passes a 160 mesh screen but is retained on a 200 mesh screen, the lower surface area results in a still thicker coating of hydrous titanium dioxide. When such flakes are incorporated in a coating composition vehicle and coated over a black surface, a golden appearance and a pleasing lustrous sparkle are seen. The golden appearance obtained with this thicker layer of hydrous titanium dioxide is a second order interference color.

Example III

The precipitation procedure used in Examples I and II, and again in this example, coats the mica flake with a translucent layer of hydrous titanium oxide. This example illustrates further the variation in color with variation in TiO_2 content per unit area together with the changes which occur on calcination of the pigment to convert the hydrous oxide coating to a more light-stable translucent coating of titanium dioxide.

A number of runs were made using the quantities of titanyl sulfate solution and mica set forth in the table below. The mica and titanyl sulfate solution used were the same as those described in Example I. All quantities are in parts by weight. The mica is dispersed in the titanyl sulfate solution, and the resulting mixture is heated to the boil and boiled under reflux for 3 hours, after which time the product is isolated by filtering, washing, and drying in the manner of Example I. The dry product is then calcined in air at about 950° C. for 1 hour. Upon cooling, shiny flakes with an iridescent sparkle are obtained. In bulk form, both the calcined and uncalcined products may be described as being off-white in appearance. However, when dispersed in a liquid and observed on a dark surface, the colors given in the table are observed. These colors vary with the amount of TiO_2 coating on the mica flakes:

Mica.....	100	100	100	100
Titanyl sulfate solution.....	772	1,160.	1,600	2,440
Equivalent TiO_2	33	50	70	105
Yield, uncalcined.....	135	155	178	210
Hydrated TiO_2 /square meter in grams.....	0.11	0.17	0.24	0.34
Color.....	Pale gold	Dark gold	Bluish violet	2nd order pale gold
Yield after calcination.....	123	140	156	182
TiO_2 /square meter in grams.....	0.085	0.14	0.19	0.27
Color.....	Very pale gold	Med. gold	Golden red	Green

From the above table, it can be seen that there is a loss in the weight of the TiO_2 coating on calcination. Such a loss is, of course, accompanied by some reduction in thickness of the film of TiO_2 and a change in the predominant hue of the interference colors. This change is in the direction of interference at a lower wave length, as is to be expected from thinner films. The calcined products of this example are much more light stable than the uncalcined products of Examples I and II.

Example IV

This example illustrates coating mica flakes using a concentrated titanyl sulfate solution of the type commonly produced during the conversion of ilmenite ore to TiO_2 pigment. Although such solutions usually contain some iron in divalent form, it is not precipitated along with the hydrous TiO_2 . Instead, the iron remains dissolved as FeSO_4 in the mother liquor.

As set forth in detail in the table which follows, 100 parts of mica as described in Example I is slurried in the indicated amount of water and heated to about 60°C . While stirring vigorously at 60°C ., the indicated amount of concentrated titanyl sulfate solution (TiOSO_4 , calculated as TiO_2 , 14.1%; FeSO_4 , calculated as Fe, 3.7%; F.A., 80) also heated to 60°C ., is added rapidly. The mixture is heated to the boil and boiling continued under reflux for the indicated time. The flakes are recovered by filtering, washing free of soluble salts and drying at 80°C . The slightly yellow nacreous flakes are then calcined in air at 950°C . for 1 hour to give slightly darker colored flakes which, when dispersed in coating compositions, impart the indicated colors to the compositions together with a lustrous iridescent sparkle in the sunshine.

	A	B
Mica.....	100	100
Water.....	236	448
Titanyl sulfate solution.....	100	365
Equivalent TiO_2	27.3	52.3
Reflux time, hours.....	2	2.5
Yield.....	130	165
Percent hydrous TiO_2	23.1	39.4
Yield after calcination.....	127	148
Percent TiO_2	21.4	35.4
Color.....	Silver	Gold

Example V

The interference color of a coated flake pigment is a function of the thickness of the coating layer thereon. Since actual measurement of this thickness is not readily done, the weight of the coating material per unit area of the surface of the substrate is a convenient index of the thickness of the coating. It is obvious that a fixed weight of coating material will produce coating of different thickness on equal weights of substrates which differ in surface area. Conversely, adjustment of the weight of substrates so that the total surface areas are equal should give equal coating and substantially equal color. The following series of samples illustrates these points using three samples of waterground white mica (muscovite) with the weights adjusted so that the total surface areas of the mica used is the same in each case.

The titanyl sulfate solution had the following composition: TiOSO_4 , calculated as TiO_2 , 14.1%; FeSO_4 , calculated as Fe, 3.7%; F.A., 80. The general procedure used to coat the mica is described in Example IV. Specific details on the procedure are as follows:

SURFACE AREA AND WEIGHT OF SAMPLES

	Sample 1	Sample 2	Sample 3
Surface area of mica, sq. meters/grams.....	3.2	2.6	2.4
Weight of mica used in grams.....	20.0	24.6	26.7
Total surface area of mica, sq. meters.....	64.0	64.0	64.0

Treatment as follows:

	Sample 1	Sample 2	Sample 3
5 a. Weight of TiOSO_4 (calc. as TiO_2), grams.....	11.7	11.7	11.7
Yield in grams.....	29.9	34.2	36.4
Weight of hydrated TiO_2 in coated flakes.....	9.9	9.6	9.7
Hydrated TiO_2 /sq. meter of mica in grams.....	0.16	0.15	0.15
10 Interference color, all three alike.....	(1)	(1)	(1)
b. Weight of TiOSO_4 (calc. as TiO_2), grams.....	15.6	15.6	15.6
Yield in grams.....	33.1	37.0	39.9
Weight of hydrated TiO_2 in coated flakes.....	13.1	12.4	13.2
15 Hydrated TiO_2 /sq. meter of mica in grams.....	0.20	0.19	0.21
Interference color, all three alike.....	(2)	(2)	(2)
c. Weight of TiOSO_4 (calc. as TiO_2), grams.....	19.5	20.8	20.8
Yield in grams.....	36.5	41.5	43.6
Weight of hydrated TiO_2 in coated flakes.....	16.5	16.9	16.9
20 Hydrated TiO_2 /sq. meter of mica in grams.....	0.26	0.26	0.26
Interference color, all three alike.....	(2)	(2)	(2)

¹ Light gold. ² Reddish gold. ³ Blue.

Example VI

In a specific examination of the particle size of the TiO_2 deposited on the mica flakes, a sample of uncalcined silver colored flake pigment may be prepared according to the following procedure which differs only in minor details from sample A in Example IV above.

100 parts of water-ground white mica (specific surface 3.2 sq. meters/gram) is slurried in 1000 parts of water and the slurry heated externally to about 95°C . At this point, 290 parts of a titanyl sulfate concentrate (15% available TiO_2 , F.A. 80) is added rapidly to the agitated slurry. The resulting slurry (temp. 89°C .) is heated to the boil and boiled 1.5 hours, cooled to 60°C ., filtered, washed free of sulfate ion and dried to give 135 parts of a yellowish silver nacreous pigment. Portions of this pigment are then calcined in air at various temperatures as shown in the table below. The final flakes, after calcination, are then examined in a conventional manner in an electron microscope and the general appearance of the samples, together with an estimate of average particle size of the TiO_2 in the metal oxide coating, is presented in the table. Three other samples prepared in a like manner and similarly examined in the electron microscope are included in the table.

Sample	Calcination temp., $^\circ\text{C}$	General appearance	Particle Size (microns)
55 This example.....	(1)	Indefinite particles, very small.	(2)
Do.....	700	Uniform discrete particles.....	0.025
Do.....	900	do.....	0.04
Do.....	1,000	do.....	0.09
Do.....	1,100	Many lath-like particles of non-uniform sizes.....	>0.10
Sample A.....	950	Discrete particles.....	0.08
Sample B.....	900	do.....	0.03
60 Sample C.....	950	do.....	0.07
Do.....	850	do.....	0.04
Do.....	950	do.....	0.07

¹ Uncalcined. ² Not measurable.

³ It should be noted that at temperatures of about 1100°C . and above the mica begins to decompose and the crystal growth of TiO_2 becomes much more rapid.

Example VII

This example illustrates the use of an organic titanate to apply a titanium oxide layer to the mica flakes.

Approximately 1 gram of muscovite mica flakes with largest dimensions of about 100 microns and with a thickness of 1-2 microns is spread in a thin layer inside a 1-inch "Vycor" tube. The tube is evacuated by means of a vacuum pump attached to one end of the tube, the other end of the tube being attached through a closed

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valve to a reservoir of tetraisopropyl titanate contained in a glass flask. The tube and flask contents are heated, with maintenance of the vacuum, to 600° C., at which temperature the valve between the tube and the organic titanate container is opened permitting the titanate vapors to pass into the hot tube. After approximately 30 minutes, the valve is closed and the tube and contents are cooled to room temperature under vacuum. After cooling, the vacuum is disconnected and the coated flakes are removed from the tube. The flakes obtained exhibit a variety of interference colors and when they are dispersed in a cellulose acetate film, they impart a nacreous appearance thereto.

Example VIII

This example illustrates improving the light stability of the hydrous titanium dioxide coating by applying an outer coating of hydrous aluminum oxide on the TiO_2 -coated mica flakes.

100 parts of the yellowish-white flakes of Example Ia is neutralized by slurrying in an excess of dilute aqueous ammonia. It is then filtered, washed, dried, if desired, and reslurried in 4000 parts of an aqueous solution containing 200 parts of $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ and 80 parts of sodium acetate. The slurry is heated to 90° C. and then held in the temperature range of 90° C.-100° C. for about 30 minutes. The slurry is filtered hot, washed with hot water until free of sulfates, and dried at about 60° C. to give a powder containing about 6% alumina (as Al_2O_3). This powder is more yellowish than the starting material, and when it is dispersed in an alkyd coating composition, such as Formulation D, and applied over a black primer, a dark golden nacreous appearance and a lustrous iridescent sparkle are obtained. When tested in a "Fade-Ometer," a cellulose acetate film (as in Formulation A) pigmented with these flakes shows a marked superiority in light stability over the untreated counterpart.

Example IX

This example illustrates a still further improvement in light stability by applying a layer of hydrous aluminum oxide to a calcined TiO_2 -coated mica flake pigment.

100 parts of the calcined product of Example III resulting from the use of 100 parts of mica and 772 parts of titanyl sulfate solution is mixed with 200 parts of an aqueous solution containing 20 parts of $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$. A 5% solution of sodium carbonate is then added slowly, while stirring, until the pH is 7.0. The flake pigment is then isolated by filtering, washed free of soluble salts, and dried. The product obtained is substantially unchanged with respect to sparkle and overall silvery gold appearance when dispersed in a coating composition vehicle and applied over a black surface. On the other hand, it exhibits a notable improvement in lightfastness. Cellulose acetate films containing the pigment show no change upon exposure in an Atlas "Fade-Ometer" for 1000 hours.

Example X

This example illustrates the use of synthetic phlogopite as the micaceous flake substrate.

20 parts of synthetic phlogopite of such particle size that all of it passes through a 160 mesh screen and is retained by a 200 mesh screen, is added at room temperature (approximately 25° C.) to 600 parts of aqueous titanyl sulfate solution containing 24 parts of titanyl sulfate calculated as TiO_2 and F.A. of 217. The mixture is stirred and diluted with 600 parts of water and then heated to 80° C. during one hour and maintained at 70-80° C. with vigorous stirring. Portions of the slurry are removed from time to time and placed in a pool of water on a black surface for determination of color. After approximately 1½ hours at 70-80° C. a blue color is evident. On continued stirring to a total of 3 hours, the color of samples taken during the stirring

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period becomes successively gold, red, blue, green, gold (again), red (again), and then, finally, green. The slurry is then filtered, and the filter cake is washed with water until the effluent wash water gives a negative test for sulfate ion. The filter cake is then washed with acetone and allowed to dry. The final product is a flake pigment having a predominant green hue and a lustrous iridescent sparkle when dispersed in an alkyd resin and viewed in the sunshine.

Example XI

This example illustrates the application of a hydrous zirconium oxide to mica flakes.

100 parts of the mica described in Example I is slurried in 2000 parts of an aqueous solution containing 200 parts of $\text{Zr}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ and previously adjusted to a pH of 2.8 by adding urea thereto. The slurry is heated to 90° C. and held near this temperature for about 2 hours with good agitation throughout. The solid product is recovered by filtering, washed, and dried, and it is then calcined for 1 hour at 700° C. in air to give a flake pigment having a silver appearance and a pleasing lustrous sparkle when dispersed in a coating composition vehicle.

Example XII

This example illustrates the application of a layer of hydrous zinc oxide to mica flakes which have been previously coated with TiO_2 .

The procedure of Example Ia is followed to produce TiO_2 -coated mica flakes and, prior to drying, 30 parts of these flakes is slurried in 2200 parts of 3% aqueous ammonium hydroxide solution at room temperature. The mixture is stirred at room temperature for 30 minutes, and then filtered. The presscake is washed with water until the pH of the effluent wash water is 8, and then dried in an oven at 80° C. 25 parts of the dried flakes is added at room temperature to a solution formed as follows: 10 parts of ZnCl_2 is dissolved in 500 parts of water, and ammonium hydroxide is then added to the solution with vigorous stirring until the precipitate initially formed redissolves. The slurry is heated to approximately 80° C. and maintained at about that temperature for about 2 hours to drive off ammonia from the solution. After the heating, the slurry is filtered and the presscake is washed free of soluble chlorides and dried at about 80° C. The product obtained has much the same appearance as the product of Example Ia. Analysis indicated the presence of 19% zinc, calculated as zinc oxide. Lightfastness of the zinc-treated product is appreciably superior to that of the corresponding product without the zinc treatment. Calcination of this zinc-containing product yields a flake pigment in which the TiO_2 is present predominantly in the rutile form, whereas in the corresponding calcined flake product which is not zinc-treated, the TiO_2 is predominantly in the anatase structure.

Example XIII

This example illustrates the application of a layer of hydrous zirconium oxide to mica flakes which have been previously coated with TiO_2 .

A TiO_2 -coated mica flake pigment exhibiting a golden color when observed on a black surface is prepared as follows: 108 parts of water-ground muscovite mica with a surface area of 3.1 square meters per gram is slurried in 600 parts of water. The slurry is heated to the boil, and 351 parts of a 20% (as TiO_2) titanyl sulfate solution (F.A. 80) is added to the boiling slurry. Heating is continued, and the mixture is refluxed for 3 hours and allowed to cool overnight before filtering. After filtering, the presscake is washed with approximately 12,000 parts of water at room temperature, then washed with about 500 parts of a 2% ammonium hydroxide solution, and finally washed with 6000 parts of water. After drying the presscake overnight at 80° C., 164 parts of flake pigment is obtained, containing approximately 34% of hydrous titanium oxide. When dispersed in a coating

composition vehicle, these flakes exhibit a reddish gold color which is more pronounced over a dark surface.

50 parts of these golden flakes is then overcoated with hydrous zirconium oxide as follows: 7.5 parts of $Zr(SO_4) \cdot 4H_2O$ is dissolved in 500 parts of water, and urea is then added slowly to the solution with good stirring to bring the pH to 2.0. 50 parts of the golden flakes is added to the solution, the resulting slurry is heated to the boil and held at the boil under reflux for 1 hour. On heating, the initial golden color of the flakes gradually changes to a purple. Addition of more of the zirconium sulfate-urea solution and further heating results in a second order gold color to the flakes. The slurry is then filtered, and the solid is washed free of sulfate and dried to give a pigment which exhibits a golden color when dispersed in a coating composition vehicle and applied over a black surface. Accelerated lightfastness tests show the zirconium-coated flakes to be appreciably better in lightfastness than the uncoated counterpart. They contain about 7.7% zirconium oxide (as ZrO_2).

The following Examples XIV to XVII, inclusive, are based upon the use of TiO_2 -coated mica flakes, made after the general procedure of Example IV, which are further coated with a second metal oxide as shown in the details. In these examples, two different samples are shown; one of these samples (flake A) is an uncalcined silver-colored flake containing about 20.7% TiO_2 . This product was prepared by treating 100 parts of the mica described in Example I with 233 parts of a titanyl sulfate concentrate containing 15% TiO_2 (F.A. about 80) (which is equal to 35 parts TiO_2). The procedure used is according to Example IV and about 126 parts of flake are obtained. Prior to drying, the residual sulfuric acid is neutralized by slurrying in an excess of dilute ammonia, filtering, and washing. The second sample (flake B) is a yellowish silver-colored flake containing about 26.2% TiO_2 made in a like manner from 100 parts mica described in Example I and 290 parts titanyl sulfate concentrate (F.A. about 80) containing 15% TiO_2 , which is equal to 43.5 parts TiO_2 .

In Examples XIV through XVIII, the term "reflex color" is used to describe the color observed at the specular angle, usually contrasting with the inherent color. In this use, it is a convenient means of distinguishing the interference color from the inherent color of metal oxide coatings.

Example XIV

This example and Example XIVa illustrate the application of a layer of chromium oxide to mica flakes which have been previously coated with TiO_2 .

$Cr(NH_2)_6Cl_3$ is prepared by dissolving 40 parts of $CrCl_3$ in liquid ammonia and allowing the excess ammonia to evaporate. The light green product thus obtained is dissolved in 2000 parts of water and then 100 parts of TiO_2 -coated mica (flake A) is added with stirring. The slurry is heated to the boil and refluxed for about 4 hours until the green color of the solution is no longer evident. The product is then isolated by filtering, washed with water, and dried. The flake pigment product is light green in color, and at the same time this green color exhibits a silvery reflex.

On calcination at 950° C. the green color becomes somewhat less intense, but the silver reflex is retained. This product, containing chromium oxide equivalent to 3.04% Cr, is markedly more lightfast than the untreated flake A.

Example XIVa

100 parts of yellowish silver flake B (26.2% TiO_2) is slurried in a solution of 40 parts chromium sulfate ($Cr_2(SO_4)_3 \cdot 5H_2O$) in 1000 parts of water at about 50° C. Borax ($Na_2B_4O_7 \cdot 10H_2O$) is then added in small increments of about 2 parts each until a constant pH of 5.5 to 6.0 is reached and maintained for at least 15 minutes. The resulting product is isolated by filtering,

washed sulfate free, and dried. After calcination for ½ hour at 900° C., the flakes are greenish gold in color with a golden reflex, and they exhibit excellent lightfastness in the cellulose acetate film of Formulation A.

Example XV

This example and Example XVa illustrate the application of a layer of iron oxide to mica flakes which have been previously coated with TiO_2 .

400 parts of silver-colored flake A (20.7% TiO_2) is added to a solution of 50 parts ferric chloride ($FeCl_3$) and 80 parts of sodium acetate ($NaC_2H_3O_2$) in 1000 parts of water at 25° C. The slurry is heated with agitation to 80° C. and stirred for one hour at 80° C. until the mother liquor is substantially colorless. A further portion of solution containing 50 parts ferric chloride and 80 parts sodium acetate in 1000 parts of water is then added. The mixture is heated for one hour at 80° C., after which time another 50 parts of ferric chloride and 80 parts of sodium acetate in 1000 parts of water is added, and the whole mixture is heated for one hour at 80° C. The slurry is filtered, washed, and dried to give yellowish-brown flakes having a golden reflex. Upon calcination at 400° C, 600° C., and 900° C., the pigment being maintained at each temperature for ½ hour, the golden reflex does not change but the overall color changes to brown at 400° C., to reddish brown at 600° C., and to a brilliant golden brown at 950° C.

Example XVa

100 parts of the yellowish silver flake B (26.2% TiO_2) is added to 600 parts of a 11.4% $FeCl_3$ solution (68 parts $FeCl_3$) and 60 parts of sodium acetate ($NaC_2H_3O_2$) is added with agitation. After the sodium acetate is dissolved, the slurry is heated to 80° C. and maintained at that temperature for several hours with frequent examination of a diluted drop of the slurry on a black surface. The overall color of the flakes is golden yellow, and the colored sparkle or reflex color progresses with continued heating through gold to red, to purple, and finally to green, while the overall golden color remains substantially unchanged. Samples are taken when each of the various colors is observed, and these samples are filtered, washed, and dried, and analyzed for iron. This analysis indicates the following iron content:

	Percent Fe
Red reflex color	8.9
Purple reflex color	11.0
Green reflex color	16.4

These samples, in addition to possessing the unusual color effects described above, show marked improvements in lightfastness as compared with the original TiO_2 -coated flakes.

Example XVI

This example and Example XVIa illustrate the application of a layer of nickel oxide to mica flakes which have been previously coated with TiO_2 .

100 parts of silver-colored flake A is added to a solution prepared by dissolving 200 parts of nickel chloride ($NiCl_2 \cdot 6H_2O$) and 500 parts of sodium acetate ($NaC_2H_3O_2$) in 2400 parts of water. The resulting slurry is heated to the boil and kept at the boil for approximately 4 hours until the flakes become light green in color. The product is then filtered, washed chloride free, and dried at about 60° C. The dried material is a light green color with a sparkling silver appearance. A portion of the dried flakes is calcined by heating to 950° C. and maintaining the flakes at this temperature for 30 minutes. The calcined product has a bright yellow color with a sparkling golden reflex. It contains 3.5% Ni. When dispersed in a vinyl composition (as in Formulation D) a particularly pleasing golden nacreous effect is obtained.

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Example XVIa

An ammoniacal nickel chloride solution is prepared by dissolving 24 parts nickel chloride ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$) in 2000 parts of water and adding concentrated ammonium hydroxide solution with constant stirring until a precipitate is formed and then redissolved. 1000 parts of silver-colored flake A ($20.7\% \text{TiO}_2$) is added, the slurry heated to the boil and maintained at the boil under reflux for about 4 hours. It is then filtered, washed free of chlorides, and dried to give light green colored flakes with a silver reflex, showing a marked improvement in light stability over the untreated silver flakes.

Example XVII

This example illustrates the application of a layer of cobalt oxide to mica flakes which have been previously coated with TiO_2 .

100 parts of silver-colored flake A is added with stirring to a solution at room temperature prepared by dissolving 200 parts of cobalt chloride hexahydrate ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$) and 300 parts of sodium acetate in 2000 parts of water. The resulting slurry is heated to the boil and kept under reflux for one hour. The slurry is then filtered hot and the presscake is washed with water until chloride free. The presscake is dried in an oven at about 80°C . The dried flakes, when dispersed in cellulose acetate as described in Formulation A produce a dry film having a gray metallic nacreous appearance. Calcination of the flakes for one hour at 950°C . results in a light green product having a silver reflex color. The product contains $2.9\% \text{Co}$.

Example XVIII

This example illustrates the application of a layer of copper oxide to mica flakes which have been previously coated with TiO_2 .

100 parts of silver-colored flake A is added to an ammoniacal copper chloride solution prepared by dissolving 20 parts of copper chloride (CuCl_2) in 1000 parts of water and then adding ammonium hydroxide ($28\% \text{NH}_3$) until a precipitate is formed and then redissolved. The slurry is gently heated at about 60°C . for one hour to drive off ammonia and precipitate a hydrous copper oxide on the mica. The flake product is then isolated by filtering, washed free of dissolved salts, and dried. The product consists of grayish flakes with a silver reflex. Calcination of a portion of the product at 950°C . for 15 minutes gives a darker gray-black product retaining the silver reflex and containing $2.4\% \text{Cu}$.

Example XIX

COPRECIPITATION WITH CHROMIUM OXIDE

40 parts of chromic sulfate ($\text{Cr}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$) is dissolved in 1000 parts of water to which is added 100 parts of water-ground white mica (Concord #300/325) and the slurry is heated, while well stirred, to 90 – 100°C . 490 parts of titanyl sulfate concentrate (TiO_2 equivalent 14.4% , F.A. 80) is then added rapidly, the slurry is reheated rapidly to the boil and maintained under reflux for about 3 hours. The product is filtered, washed free of soluble salts and dried to give greenish flakes with a reddish gold reflex color. On calcination at about 900°C , the product is transformed to yellow nacreous flakes with a brilliant gold reflex color. Coating compositions containing this pigment exhibit excellent lightfastness.

Example XX

COPRECIPITATION WITH IRON OXIDE

100 parts of Concord Water Ground Mica #200/325 is slurried in 920 parts of a titanyl sulfate solution (TiO_2 equivalent 4.15% F.A. 220) into which is dissolved 20 parts of anhydrous ferric sulfate. The slurry is thoroughly agitated and heated to 95 – 100°C . in about 30 minutes and held at that temperature for about 4 hours. Samples of the slurry taken during the heating period

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and diluted with water on a black surface show a progressive change in the color of the mica flakes suspended therein. The final pigment is filtered, washed free of soluble salts and calcined for one hour at 900°C . to give a yellow nacreous flake pigment which produces a strongly golden color in a coating composition. Such compositions exhibit a very high degree of lightfastness.

Example XXI and XXII

The following examples illustrate the use of mixtures of the new nacreous flake pigments with conventional colored pigments to obtain highly attractive decorative effects.

(Example XXI)

ACRYLIC LACQUERS WITH MIXTURES OF PIGMENTS

These lacquers are based upon a vehicle blend consisting of

	Percent
Mixed acrylic ester polymer (Acryloid A-101)-----	85.4
Butyl benzyl phthalate (as plasticizer)-----	14.6

and a solvent blend consisting of

	Percent
Monoacetate of ethylene glycol monoethyl ether-----	20
Methyl ethyl ketone-----	30
Toluene-----	50

A copper phthalocyanine (CPC) blue acrylic lacquer (made in a conventional manner in a ball mill) consists of

	Parts
Copper phthalocyanine blue-----	3.2
Vehicle blend-----	66.2
Solvent blend-----	30.6

The following mixed lacquers are then made:

	A, parts	B, parts
Silver flake pigment (Example Va)-----	4.75	4.75
Vehicle blend-----	97.0	97.0
CPC blue lacquer-----	7.8	1.6
Solvent blend-----	21.7	21.7

The ingredients are thoroughly blended by high speed agitation for 15 minutes, thinned with additional solvent blend to spraying consistency and sprayed with 3 double coats on a suitable panel.

In lacquer A, the silver flake/blue ratio is 95/5 and the resulting panel exhibits a highly pleasing "metallized" effect with a more pronounced sparkle than usually exhibited by lacquers containing aluminum flake. The effect is obtained over a fairly wide range of flake/color ratios up to as much as about 50/50.

In lacquer B, the silver flake/blue ratio is 99/1 and the resulting panel exhibits the effect of a bluish toned pearl with a brilliant iridescent sparkle under bright illumination.

(Example XXII)

ALKYD ENAMEL WITH A MIXTURE OF PIGMENTS

A polychloro copper phthalocyanine green (CPC green) enamel of the following composition is prepared by dispersion in a ball mill in the conventional manner

	Parts
CPC green pigment-----	5.0
Non-oxidizing coconut oil-modified alkyd resin solution (16% solids)-----	42.6
Modified melamine formaldehyde resin (55% solids)-----	20.0
Aromatic hydrocarbon solvent-----	16.2
Aliphatic hydrocarbon solvent-----	16.2

A portion of this enamel is mixed with a nacreous flake pigment as follows:

	Parts
Gold flake pigment (Example Vb)-----	4.75
CPC green enamel-----	5.00
Non-oxidizing coconut oil-modified alkyd resin solution (60% solids)-----	58.4

These ingredients are mixed for 5 minutes by high speed agitation after which 27.2 parts of modified melamine formaldehyde resin (55% solids) is added and high speed agitation is continued for 5 minutes. The enamel is then reduced to spraying consistency with a 50/50 aromatic/aliphatic hydrocarbon mix and sprayed with 3 double coats onto a suitable panel. This enamel contains a gold flake/CPC green ratio of 95/5 and the color is much yellower than that of the CPC green enamel alone. In addition, the panels exhibit a lustrous golden sparkle.

The pigments described in the foregoing specification offer the following notable advantages:

- (1) They can be prepared and marketed as dry pigments.
- (2) These dry pigments show a remarkable ease of dispersion in the compositions in which they are used.
- (3) They show a nacreous effect of a degree not readily produced with prior art nacreous pigments.
- (4) They show an iridescent sparkle with a pronounced predominant hue which may be varied at will by simple alterations in the compositions.
- (5) When properly stabilized, they offer a high degree of lightfastness.
- (6) They exhibit substantial freedom from toxicity.
- (7) They are chemically stable and do not contribute to water spotting of surface finishes with compositions containing them.
- (8) They are heat stable and can be used in baking enamels and in plastics processed at high temperature.
- (9) They are completely non-bleeding in solvents and in the usual chemical agents to which coating compositions may be subjected.
- (10) They are compatible with coating composition vehicles and plastic systems.
- (11) They make possible tinctorial effects not heretofore obtainable.

Since it is obvious that many changes and modifications can be made in the above-described details without departing from the nature and spirit of the invention, it is to be understood that the invention is not to be limited to said details except as set forth in the appended claims.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A pigment composition consisting essentially of translucent micaceous flakes having on the surface thereof a translucent layer of metal oxide particles consisting essentially of particles selected from the group of hydrous titanium dioxide particles, titanium dioxide particles, hydrous zirconium dioxide particles, and zirconium dioxide particles, substantially all of which are less than 0.1 micron in particle size, said layer having a thickness of about 20-250 millimicrons, said pigment being silver color when the thickness of metal oxide layer is in the lower portion of said range and exhibiting various colors of the spectrum as the thickness of the metal oxide layer is increased.

2. The composition of claim 1 in which the thickness of the metal oxide layer is 20-155 millimicrons.

3. The pigment composition of claim 1 wherein the micaceous flakes are white mica flakes having a specific surface area of 2-7 square meters per gram.

4. A pigment composition consisting essentially of translucent micaceous flakes having on the surface thereof translucent, successive layers of metal oxides, the first layer being a layer of a metal oxide from the group consisting of hydrous titanium dioxide particles, titanium dioxide particles, hydrous zirconium dioxide particles, and zirconium dioxide particles, substantially all of which are less than 0.1 microns in particle size, the weight of the metal oxide in said first layer being about 10-66% by weight of the total pigment, and on top of said first layer at least one layer of a different metal oxide from the group consisting of TiO_2 , ZrO_2 , Al_2O_3 , ZnO , Sb_2O_3 , SnO_2 , Fe_2O_3 , CuO , NiO , CoO , and Cr_2O_3 , and the hydrous

forms of these oxides, said different metal oxide being in the form of particles substantially all of which are less than 0.1 micron in particle size, the amount of said metal oxide being 0.5 to 20% by weight of the metal oxide in the first layer.

5. The pigment composition of claim 4 wherein the first layer is titanium dioxide and on top of said layer of titanium dioxide is a layer of Cr_2O_3 .

6. The pigment composition of claim 4 wherein the first layer is titanium dioxide and on top of said layer of titanium dioxide is a layer of Fe_2O_3 .

7. The pigment composition of claim 4 wherein the first layer is titanium dioxide and on top of said layer of titanium dioxide is a layer of NiO .

8. The pigment composition of claim 4 wherein the first layer is titanium dioxide and on top of said layer of titanium dioxide is a layer of Al_2O_3 .

9. A pigment composition consisting essentially of a translucent micaceous flake substrate having on the surface thereof a translucent layer consisting essentially of a colorless metal oxide selected from the group of titanium dioxide, zirconium dioxide, and the hydrated forms thereof, said composition being a colored nacreous flake pigment exhibiting, under bright illumination, a lustrous sparkle with a predominant color varying, with increasing thickness of the metal oxide layer, from silver to gold to red to blue to green.

10. The composition of claim 9 having deposited on the surface thereof a translucent layer of a second metal oxide.

11. A pigment composition consisting essentially of translucent micaceous flakes having on the surface thereof a translucent layer of metal oxide particles, the major amount of said metal oxide particles being a metal oxide from the group consisting of titanium dioxide, zirconium dioxide, and the hydrous forms thereof wherein substantially all of said particles are less than 0.1 micron in particle size and the amount of said oxide is 10-66% by weight of the total pigment, and intermingled therewith a minor amount of different metal oxide particles in which the metal oxide is selected from the group consisting of TiO_2 , ZrO_2 , Al_2O_3 , ZnO , Sb_2O_3 , SnO_2 , Fe_2O_3 , CuO , NiO , CoO , Cr_2O_3 , and the hydrous forms thereof, said different metal oxide being in the form of particles substantially all of which are less than 0.1 micron in particle size, the amount of said metal oxide being 0.5 to 20% by weight of the metal oxide present in the major amount.

12. The pigment composition of claim 11 in which titanium dioxide constitutes the major amount of the metal oxide layer and Cr_2O_3 constitutes the minor amount of the metal oxide layer.

13. The pigment composition of claim 11 in which titanium dioxide constitutes the major amount of the metal oxide layer and Fe_2O_3 constitutes the minor amount of the metal oxide layer.

14. A pigment composition consisting essentially of white mica flakes having on the surface thereof a translucent layer of titanium dioxide particles substantially all of which are less than 0.1 micron in particle size, said layer having a thickness of 20-90 millimicrons, said pigment being of a silver color when the thickness of the metal oxide layer is in the lower portion of said range and progressing to a gold color as the thickness of the metal oxide layer is increased.

15. The composition of claim 9 wherein the colorless metal oxide is titanium dioxide.

References Cited in the file of this patent

UNITED STATES PATENTS

834,739	Lillienfeld	Oct. 30, 1906
2,332,220	Harshberger	Oct. 19, 1943
2,941,895	Haslam	June 21, 1960
2,995,459	Soloway	Aug. 8, 1961
3,008,844	Grunin et al.	Nov. 14, 1961

United States Patent [19]

Esselborn et al.

[11] 4,086,100

[45] Apr. 25, 1978

[54] RUTILE-CONTAINING LUSTROUS PIGMENTS

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[21] Appl. No.: 754,698

[22] Filed: Dec. 27, 1976

Related U.S. Application Data

[63] Continuation of Ser. No. 616,843, Sep. 25, 1975.

[30] Foreign Application Priority Data

May 22, 1975 Germany 2522572

[51] Int. Cl.² C09C 3/06; C09C 1/36

[52] U.S. Cl. 106/291; 106/300

[58] Field of Search 106/291, 300

[56] References Cited

U.S. PATENT DOCUMENTS

2,316,841	4/1943	Cole	106/300
3,087,828	4/1963	Linton	106/291
3,342,617	9/1967	Jackson	106/291
3,627,553	12/1971	Clark et al.	106/291 X
3,634,119	1/1972	Klenke	106/291
3,650,790	3/1972	Klenke et al.	106/291
3,711,308	1/1973	Brand et al.	106/291

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[57] ABSTRACT

Mica flake-based lustrous pigments having a plurality of TiO₂ and SnO₂ layers thereon comprising at least one succession of rutile/SnO₂/rutile have improved properties, including light and weathering fastness.

16 Claims, No Drawings

RUTILE-CONTAINING LUSTROUS PIGMENTS

This is a continuation of application Ser. No. 616,843, filed Sept. 25, 1975.

BACKGROUND OF THE INVENTION

This invention relates to lustrous mica-flake pigments coated with TiO_2 and SnO_2 .

A whole series of mica flake-based lustrous pigments coated with metal oxides has been known, e.g. from U.S. Pat. Nos. 3,087,828; 3,087,829; and 3,711,308; German patent specification No. 2,009,566 and German published specification No. 2,214,545. However, for special purposes, the light fastness and the weathering resistance of all of these pigments leaves something to be desired due primarily to the fact that in these pigments the TiO_2 is present in the anatase modification which is evidently favored by the mica substrate.

There are also known mica flake-based lustrous pigments which contain both TiO_2 and SnO_2 . The tin oxide is either present as a surface coating on a TiO_2 coating or as a mixed precipitate with TiO_2 . See, e.g., German patent specification No. 1,467,468. X-ray investigation of such pigments shows that the TiO_2 , in spite of its tin content, is present in the anatase modification. According to published German specification No. 2,214,545, pigments are preferred in which the metal oxide layer consists preponderantly of rutile TiO_2 plus a small amount of tin oxide, with the concentration of the tin oxide being greater in the regions closest to the mica. The SnO_2 content of the metal oxide layer is preferably 0.5 to 5 wt. % but in no case to more than 20 wt. %. However, it has been found that these pigments contain TiO_2 which is not completely and not reproducibly in the rutile form but instead is very frequently present at least partially in the anatase form, although it is stated in published German patent specification No. 2,214,545 that the TiO_2 was present "substantially in rutile form."

Thus, it has been known for some time that, on the one hand, SnO_2 acts as catalyst for the conversion of anatase into rutile and that, on the other hand, mica favors the formation of the anatase modification of the TiO_2 . Nevertheless, a satisfactory solution to the problem of producing rutile-containing pigments does not exist.

It is an object of this invention to provide lustrous pigments based on mica flakes coated with TiO_2 having improved properties in which the TiO_2 is present completely and reliably as rutile, even if the pigments have a comparatively thick layer of TiO_2 exhibiting interference colors. It is another object of this invention to provide such pigments which, compared to comparable pigments in which the anatase modification is present, display considerable technical advantages in use, including better light and weathering fastness. It is still another object to provide processes for the production and use of such pigments. Other objects will become apparent to those skilled in the art.

SUMMARY OF THE INVENTION

According to this invention, there are provided mica flake-based pigments with improved properties having a succession of metal oxide layers on the mica flakes, consisting essentially of TiO_2 and SnO_2 , said pigments being characterized by the feature that the layers alternate and consist at least of the sequence rutile/ SnO_2 /rutile. In addition, said metal oxide layers, especially

the SnO_2 layers, can optionally contain aluminium oxide.

DETAILED DISCUSSION

Such pigments have hitherto not been described. The arrangement of the metal oxide layers according to this invention is critical to the improved properties of the novel pigments. Surprisingly, the first layer, i.e., the TiO_2 layer directly in contact with the surface of the mica flakes must have a very small thickness, i.e., no more than about 25 nm., in order to provide satisfactory rutile pigments. In general, the layer thickness is from 0.1 to 25 nm. However, even thinner layers which are too thin to be measured with accuracy, are sufficient to provide pigments with satisfactory rutile layers. Admittedly, the TiO_2 layer directly in contact with the surface of the mica is still subject to the anatase-inducing influence of the mica, but evidently provides an acceptable and uniform covering of the mica surface which is a prerequisite for a uniform and acceptable SnO_2 coating. According to X-ray analysis, upon calcining, the TiO_2 layer is converted completely into rutile.

To the titanium hydroxide-coated mica flakes is then applied an intermediate layer of SnO_2 , preferably of a thickness of about 2 to 25 nm. This SnO_2 layer, in an especially preferred embodiment, consists solely of SnO_2 or, optionally, like the TiO_2 layers, can contain certain amounts of Al_2O_3 or a hydrated form thereof, e.g., up to about 10%, preferably up to about 7%, of the total metal oxide content of the SnO_2 layer.

The total amount of SnO_2 in the rutile/ TiO_2 /rutile layers is preferably 5 wt. % or more, preferably about 8 to 30 wt. % of the total metal oxide content of the alternating rutile/ SnO_2 layers. SnO_2 contents of up to 90 wt. % are technically possible but usually are uneconomical.

Over the SnO_2 layer is then provided a further layer of TiO_2 , which in the final pigment, like the first TiO_2 layer is completely in the form of rutile. This, or a like rutile layer if further intermediate metal oxide layers are provided, is preferably the top or covering layer. The thickness of this layer depends solely upon the desired interference color of the pigment. As a rule, it varies from about 20 to 200 nm. However, this range is not limiting since only the color is affected by the thickness. Thus, in principle, any amount or layer thickness can be deposited which is conventional for TiO_2 -coated mica pigments, many of which are commercially available.

According to this invention a plurality of tin oxide layers, alternating between TiO_2 layers, can be applied to the mica flakes so that a multiple sandwich structure results. In this case, the interference color of the pigment is determined by the total construction of the metal oxide layers. The amounts of oxide, i.e., the layer thicknesses, necessary therefor are determined by the refractive index of the oxides and can be calculated according to known rules. It is essential, however, that the bottom layer in contact with the mica flake be a thin TiO_2 layer. As the top or covering layer either a rutile or an SnO_2 layer can be employed but a rutile layer is preferred. As stated above, all or any of the individual oxide layers can have an Al_2O_3 content.

In a process aspect, this invention relates to a process for the production of such pigments which comprises coating uncoated mica flakes first with a thin layer of titanium hydroxide or a hydrate thereof; then depositing onto the thus-coated mica flakes a layer of tin hydroxide from a tin II salt solution in the presence of an

oxidation agent; and then depositing another titanium hydroxide layer onto the coated mica flakes from a titanium salt solution. Optionally, any or all of these steps can be conducted in the presence of a soluble aluminum salt, thereby co-precipitating a hydrated form of aluminium oxide. Optionally also, the latter two coating steps can be repeated one or more times, in the same sequence. Thereafter, the mica flakes are washed, dried and calcined in the conventional manner.

The coating of the mica flakes can be accomplished according to conventional methods. The mica to be coated is normally slurried in deionized water and brought to an elevated temperature, e.g., about 40° to 90° C. The first thin TiO₂ layer is then deposited by precipitation of titanium hydroxide or a hydrate thereof from titanium salt solutions, e.g., from titanyl sulphate or titanium chloride. The reaction conditions are described in the literature, e.g., in German patent specification No. 2,009,566. This first TiO₂ layer should be as thin as possible in order to provide a pigment which contains roentgenographically pure rutile. The amount of titanium salt necessary for the selected mica surface can be calculated in the usual way. The coating operation is stopped when the desired layer thickness, up to a maximum of 25 nm., is reached.

Next, the tin hydroxide is deposited on the thus-coated mica. Contrary to the statements in the previously published literature, the coating of the mica flakes coated with TiO₂, with the formation of lustrous pigments, is accomplished best not with Sn IV salt solutions but instead with Sn II salt solutions in the presence of an oxidation agent. It is evidently important for this process that the oxidation occurs only slowly and during the precipitation. Under these conditions, one obtains, surprisingly, smooth tin dioxide hydrate layers with a previously unachievable uniformity.

It has been found, surprisingly, that for the achievement of satisfactory layers, the presence in the precipitating bath of a small amount of a soluble aluminium salt from which Al₂O₃ is subsequently formed, is desirable. Although the influence of the aluminium ions and/or of the aluminium oxide or its hydrate cannot be completely explained, three phenomena are especially worth mentioning. Surprisingly, the co-precipitation of aluminium hydroxide with the Ti or Sn hydroxide prevents crack formation which frequently appears when tin dioxide hydrate layers of high water content are calcined. Also, the addition of the aluminium salts appears to promote the formation of smooth tin dioxide layers and the quantitative deposition of the precipitates on the mica surface.

For the deposition of the tin oxide layer, the suspension containing mica flakes coated with a TiO₂ hydrate is adjusted by the addition of an acid, e.g., hydrochloric acid, to a pH value of 0.5 to 3.0, preferably about 1.0 to 2.5. The addition of the tin salt solution is then conducted in such a manner that the precipitate is deposited immediately and quantitatively as it forms. Thus, per unit time, there can be supplied to the mica slurry only such amount of the salt solutions to the reaction which the surface to be coated can take up per unit time. This is conveniently achieved by adding an aqueous solution of the tin salt slowly to the warmed suspension of the mica flakes. The acidity of the aqueous solution of the tin salt is adjusted in the usual manner, e.g., with hydrochloric acid, to a molarity of acid of between about 0.1 and 5.

As soluble tin salts, especially preferred are tin II chloride and tin II sulphate. However, the anion is not critical. The concentration of the tin II salt solution can be varied over a wide range but generally for reasons of expediency, is preferably from 0.1 to 3 moles per liter.

The tin salt solution optionally and preferably contains a water-soluble aluminium salt, e.g., aluminium chloride, acetate, nitrate and sulphate, as well as alkali metal aluminium mixed salts, e.g., potassium, sodium and ammonium aluminium sulphate. Preferably, about 0.01 to 2 moles Al per mole Sn⁺² is present, more preferably about 0.1 to 1 mole. It will be apparent that the aluminium salt can be added concurrently as a separate salt solution. If aluminium salts are added to the mica flake slurry, both metal ions should, in any case, be present simultaneously in the solution during the precipitation. Surprisingly, the desired effects are also achieved even in the presence of only trace amounts of Al ions. This is all the more surprising since only a very small part of the Al ions present in the case of the precipitation or formation of the hydrolysis products is incorporated into the pigment. Whereas the tin ions are deposited quantitatively on the mica flakes, a quite considerable part of the Al ions remains behind in the precipitation solution. This residual ionic Al can be found by back titration, e.g. in amounts of up to 96% of the Al salt used, from the aqueous phase after removal of the mica flakes. This applies similarly to the addition of aluminium ions to the titanium salt solutions. Methods for such additions are per se known. The Al₂O₃ content of the TiO₂ layers is not critical. However, not only the salt solution for the precipitation of the first thin TiO₂ layer but also those employed for the deposition of subsequent layers or any one thereof, preferably contain small amounts of water-soluble aluminium salts which co-precipitate to provide Al₂O₃ in the final metal oxide layer. If Al ions are present during the formation of the SnO₂ layer, the addition of more Al salts is not required to supply Al₂O₃ to subsequent oxide coatings because of residual Al ions present in the precipitation solution. These Al salts can be added to the titanium and tin salt solutions prior to the precipitation step or can be added separately and concurrently therewith to the mica flake slurry.

The deposition of the hydrated tin oxide is carried out in the presence of an oxidation agent, which can be present in the salt solution or added separately and concurrently therewith to the slurry. Oxidation agents which can be employed are those which oxidize Sn (II) ions into Sn (IV) ions, e.g., air, oxygen, H₂O₂ and hypochlorites. Especially useful are hydrogen peroxide and chlorates, especially potassium chlorate. The oxidation agent is expediently added in amounts about chemically equivalent to the tin salt solution employed. However, the concentrations and amounts are not critical and, if desired, atmospheric oxygen for the oxidation can be additionally introduced by the stirring of the slurry. Therefore, the oxidation agent can also be added in an excess or in a deficient amount. The optimum conditions in each case can easily be ascertained by routine experiments. Expediently, the aqueous solution of the oxidation agent is added separately from but simultaneously with the metal salt solution. It is normally preferable to avoid the introduction, by the oxidation agent, of further foreign ions, which may adversely influence the reaction.

It is expedient to maintain the pH value as constant as possible during the whole period of precipitation. This

can be accomplished by the slow addition of, e.g., aqueous alkali metal hydroxide or ammonium hydroxide, preferably dilute aqueous sodium hydroxide solution or gaseous ammonia, as needed.

The production of the rutile pigments according to the invention and their quality depends in great part upon the special coating process by which the tin hydroxide is deposited. Hitherto, the coating with uniform SnO_2 layers and thus the dependable production of pure rutile pigments was not possible.

For pigments with only 3 metal oxide layers, the subsequent color-imparting TiO_2 layer is deposited in the desired layer thickness according to conventional methods, preferably after an interval of about 10 to 60 minutes after completion of the tin salt addition, in order to ensure complete hydrolysis of the tin salts. For details of the reaction conditions, see German patent specification No. 2,009,566, whose disclosure is incorporated by reference. The deposition takes place in the same way as the deposition of the first TiO_2 layer, e.g., employing titanium salt solutions at pH values of from 0.5 to 5.0 and at temperatures from about 50 to 100° C., the only difference being that the thickness of the layer can and preferably does exceed 25 nm. so as to produce a pigment with an interference color. Upon reaching the desired layer thickness, the coating operation is discontinued. During the coating, the color scale known from conventional lustrous pigments is passed through with increasing layer thickness, as illustrated below.

Thickness of 2nd TiO_2 Layer in nm	Interference Color
about 40	silver
about 55	yellow
about 85	red
about 95	violet
about 130	blue
about 150	green

With still thicker layers, colors of higher order appear. In the case of pigments with more than 3 layers, the Ti- and Sn-containing layers continue to be deposited alternately. In each case, reaction conditions which are known in the art can be employed.

All precipitations are so carried out that, in each case, temperature and pH value are kept as constant as possible during the whole coating operation. Furthermore, the addition of the reaction components is at a rate such that hydrated titanium or tin oxide is deposited immediately and quantitatively on the mica flakes as it is precipitated. Thus, per unit time, only such an amount of the reactants is supplied to the reaction which the surface of the mica to be coated can take up per unit time. Preferably, the various depositions are carried out successively, without isolation of the resulting intermediate coated products, although, in principle, a separation, washing and conceivably also calcination of the products is possible after each deposition. However, such isolations generally are omitted for economic reasons. The deposition of the various alternating layers is conducted in the same manner, with the final covering layer being either TiO_2 or SnO_2 but preferably the former.

The coated mica flakes are separated in the usual way from the slurry, are thoroughly washed with water and then dried. The coated mica flakes are then subjected to a conventional calcination process, e.g., for about 10 minutes up to about 4 hours at temperatures of up to about 1100° C., preferably from about 600° to 1000° C.

After this treatment, one obtains rutile pigments, the X-ray analysis of which no longer shows anatase lines.

The new pigments according to the invention can be produced from mica flakes conventionally employed for this purpose. The most frequently employed mica is muscovite. As a rule, the mica flakes have a diameter of about 5 to 200 microns and a thickness of about 0.1 to 5 microns, preferably about 0.5 micron.

Depending on the desired color shade, the new pigments contain metal oxide layers on the mica flakes in a total thickness of about 20 to about 200 nm., corresponding to a metal oxide content for the coated flakes of about 10 to about 90 wt. %. As a rule, pigments with a metal oxide content substantially lower than 5 wt. % do not possess the desired lustrous quality. An accurate determination of the aluminium oxide content of the metal oxide layer is for all practical purposes not possible since aluminium is also contained in the mica itself. The precise Al_2O_3 content in the metal oxide layer is not critical. Instead, it is the presence of Al ions during the precipitation of the hydrolysis products formed from the tin salts which appears essential to the improved results achieved. From the values obtained in the case of back titration, it can, however, be deduced that the proportion of Al_2O_3 in the SnO_2 layer of the final pigment varies from traces, e.g., 0.001 wt. %, to about 10%, with 7% ordinarily not being exceeded.

Typical examples of the pigments of this invention have the following composition:

Mica Flake Pigments	Metal Oxide Coating
25 to 90 wt. % mica	0 to 10 wt. % Al_2O_3
7 to 70 wt. % TiO_2	60 to 95 wt. % TiO_2
(rutile)	
3 to 25 wt. % SnO_2	5 to 30 wt. % SnO_2

However, depending on the selected thickness of the respective metal oxide layers, pigments of this invention can also be obtained whose analyses vary considerably from the above values.

The pigments of this invention can be employed in the same manner as known mica flake pigments. They are especially suited for those fields of use where light fastness is of primary importance, e.g., motor car lacquers, and in cosmetics, where definite and very differentiated color nuances are desired. They are also well suited for the coloring of synthetic resins. The concentration thereof in the final compositions varies, depending upon the field of use, over a wide range, e.g., between 0.1 and 80%.

They can also be employed as starting materials for the production of other lustrous pigments. For example, the novel pigments can advantageously be coated in per se known manners with one or more further layers, e.g., with silicates, iron oxides, chromium oxides, Al_2O_3 , zirconium dioxide, as well as dyestuffs and/or colored lakes, especially Al colored lakes.

Without further elaboration, it is believed that one skilled in the art can, using the preceding description, utilize the present invention to its fullest extent. The following preferred specific embodiments are, therefore, to be construed as merely illustrative, and not limitative of the remainder of the disclosure in any way whatsoever.

EXAMPLE 1

60 g. of muscovite (diameter of 20 - 40 μ) are suspended in 1.5 liters of completely deionized water. The pH of the suspension is brought to 2.2 with dilute hydrochloric acid. The suspension is then heated to 75° C. To the heated slurry is slowly added with stirring 30 ml. of a solution of 150 g. TiCl₄ and 50 g. HCl per liter (solution I), simultaneously with a 15% aqueous sodium hydroxide solution at a rate which maintains the pH constantly at 2.2. About 10 minutes after the addition is completed, 300 ml. of a tin chloride solution (19.1 g. SnCl₂·2H₂O per liter of 5% hydrochloric acid, solution II) is slowly added to the slurry with stirring, simultaneously with 300 ml. of a potassium chlorate solution (4.3 g. KClO₃ per liter) and a 15% aqueous sodium hydroxide solution so as to keep the pH value constantly at 2.2.

About $\frac{1}{2}$ hour after the addition is complete, about 270 ml. of solution I is again added while keeping the pH value constant. The pigment acquires a strong, silvery luster. The coating operation is discontinued and the suspension is further stirred for about 1 hour at 75° C. Then the pigment is filtered off, washed free of salts with completely deionized water, dried and calcined at 950° C. for half an hour. The pigment displays a strong, silvery luster. X-ray analysis shows that the TiO₂ is present in rutile form only. The pigment consists of 72.4% mica, 23.0% TiO₂ and 4.6% tin dioxide.

EXAMPLE 2

The following solutions are employed:

Solution I: A solution of titanium tetrachloride in hydrochloric acid (15% TiCl₄ and 4% HCl);

Solution II: A solution of 38.2 g. SnCl₂·2H₂O in 1000 ml. 5% hydrochloric acid; and

Solution III: A solution of 8.3 g. KClO₃ in 1000 ml. water.

60 g. of muscovite (diameter 10 - 40 μ) are suspended in 2 liters completely deionized water and the pH value of the suspension adjusted to 2.2 with Solution I. The suspension is heated to 70° C. While stirring, 30 ml. of Solution I are slowly added simultaneously with a 15% aqueous sodium hydroxide solution at a rate which maintains the pH value of the slurry at a constant 2.2. After about $\frac{1}{2}$ hour after completion of the addition of Solution I, during which time stirring is continued, Solution II and Solution III are slowly run in simultaneously at about the same rate, while maintaining the pH value constant at 2.2 with 15% aqueous sodium hydroxide solution. About $\frac{1}{2}$ hour after completion of the addition, Solution I is again added in the same manner as the first coating operation. During this coating step, the mica flakes exhibit various interference colors, depending on the amount of Solution I added. Upon reaching the blue interference color (about 800 ml. of Solution I), the coating operation is stopped. The suspension is then stirred for about 1 hour. The pigment is filtered off, washed with water, dried and calcined for 30 minutes at 950° C. Roentgenographic investigation

shows that the TiO₂ layer has only the rutile form. The pigment exhibits very good luster and luminescent color power. It contains 50.4% mica, 43.1% TiO₂ and 6.5% SnO₂.

EXAMPLE 3

60 g. of muscovite with a flake diameter of about 10 - 50 nm. are suspended in 1 liter completely deionized water. The suspension is adjusted to pH 2.2 with dilute hydrochloric acid. After heating to 75° C., titanium hydroxide is first deposited on the flakes employing 30 ml. of a solution of 150 g. of TiCl₄ in 1000 ml. of 5% hydrochloric acid in the manner described above, keeping the pH value at a constant 2.2 with 15% aqueous sodium hydroxide solution. Subsequently, a layer of tin hydroxide is so deposited on the mica flakes by adding 300 ml. amounts of 10% hydrochloric acid containing tin II chloride at a concentration shown in Table I simultaneously with a like volume of KClO₃ solution of equivalent concentration as shown in Table I at the same flow in rate, again maintaining the pH value at a constant 2.2 by the simultaneous addition of 15% aqueous sodium hydroxide solution. About 20 minutes after the addition is completed, the flakes are then coated with titanium hydroxide in the same manner as the first coating step employing 270 ml. of a solution of 150 g. TiCl₄ in 1000 ml. of 5% hydrochloric acid, again maintaining the pH value at a constant 2.2 by the simultaneous addition of 15% aqueous sodium hydroxide solution.

After conclusion of the coating operation, the coated mica flakes are filtered off, washed with completely deionized water, dried at 100° C. and subsequently calcined at 950° C. for 30 minutes. The pigments exhibit a strong silvery luster. In all cases, the TiO₂ is present solely in rutile form (roentgenographic detection). Table I is a summary of the coating conditions and the composition of the pigments thus-obtained.

TABLE I

Experiment	Concentration of SnCl ₂ Solution (SnCl ₂ ·2H ₂ O in g/l.)	Concentration of KClO ₃ Solution in g/l.	Composition of the Oxide Layers		
			Inner Layer (% TiO ₂)	Middle Layer (% SnO ₂)	Outer Layer (% TiO ₂)
A	19.1	4.3	8	17	75
B	28.6	6.0	8	23	69
C	38.2	8.6	7	29	64

EXAMPLE 4

Analogously to Example 3, muscovite is coated with 3 successive layers of titanium hydroxide, tin hydroxide and titanium hydroxide, in a series of experiments in which the pH is maintained at other constant values during the tin hydroxide precipitation. The coating conditions, insofar as they vary from those of Example 3, are summarized in Table II. In all cases, there is obtained a strongly glossy silver pigment, which contains TiO₂ solely in rutile form.

TABLE II

TABLE II							
Coating with Tin Hydroxide							
Experiment	pH	Concentration of SnCl_2 Solution ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, g/l.)	Amount of SnCl_2 Solution (ml.)	Concentration of HClO_3 Solution (g/l.)	Composition of the Oxide Layers		
					Inner Layer (% TiO_2)	Middle Layer (% SnO_2)	Outer Layer (% TiO_2)
D	2.2	19.1	300	4.3	8	17	75
E	1.8	19.1	300	4.3	8	17	75
F	1.5	19.1	300	4.3	8	17	75
G	1.0	19.1	300	4.3	8	17	75

EXAMPLE 5

Analogously to Example 3, in a series of experiments pigments are prepared in which the two TiO_2 layers vary in layer thickness. The same solutions are employed as in Example 3 but the volume of the solutions used for the two coating steps is varied. Also, the tin hydroxide coating step is conducted at a pH value of 1.5. In all cases, silver pigments are obtained with very good gloss and which contain the TiO_2 solely in rutile form.

Table III is a summary of the experimental conditions employed and the composition of the pigments obtained.

TABLE III

TABLE III									
Experi- ment	1st Coating with Titanium Hydroxide			2nd Coating with Titanium Hydroxide			Composition of the Oxide Layers		
	pH	Amount of TiCl ₄ Solu- tion, ml.	Coating with Tin Hydroxide pH	pH	Amount of TiCl ₄ Solu- tion, ml.	Inner Layer (% TiO ₂)	Middle Layer (% SnO ₂)	Outer Layer (% TiO ₂)	
H	2.2	60	1.5	2.2	240	17	17	66	
I	2.2	30	1.5	2.2	270	8	17	75	
K	2.2	15	1.5	2.2	285	4	17	79	

EXAMPLE 6

Analogously to Experiment A described in Example 3, muscovite is coated with 3 successive layers of titanium hydroxide, tin hydroxide and titanium hydroxide, except that instead of the KClO_3 solution, there is used as oxidation agent a chemically equivalent amount of 5% hydrogen peroxide. The pigment obtained exhibits an excellent luster, a silvery color and contains the TiO_2 solely in rutile form. The analysis data agree completely with those of the product according to Experiment A.

EXAMPLE 7

5.0 kg. of muscovite with a particle diameter of about 10 to 40 μ are suspended in 100 liters of completely deionized water. The pH is adjusted to 2.1 with dilute hydrochloric acid. The suspension is heated to 75° C. and with stirring there is added 2.5 liters of an aqueous solution of 150 g TiCl_4 and 40 g. HCl per liter, over a period of 20 minutes, simultaneous with a 30% aqueous sodium hydroxide solution at a rate which maintains the pH value at a constant 2.1. Subsequently, a solution of 162 g. KClO_3 in 2.5 liters of water is added and a solution of 717 g. $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ in 2.86 liters concentrated hydrochloric acid in 21.8 liters water is passed in at a rate of about 10 liters/hour, concurrently with 30% aqueous sodium hydroxide solution at a rate which keeps the pH value at a constant 2.1. The slurry is allowed to

stand for about 30 minutes and the final titanium hydroxide coating is applied, employing a solution of 150 g. TiCl_4 and 50 g. HCl per liter, again keeping the pH value at 2.1 with 30% aqueous sodium hydroxide solution. During the coating, the pigment acquires a strong silver gloss, whereupon the coating operation is stopped. The slurry is filtered as usual, the mica flakes washed and dried and subsequently calcined at 960° C. for 35 minutes. Roentgenographic investigation reveals that the TiO_2 is present solely in the rutile form. The product contains 68% mica, 26% TiO_2 and 6% SnO_2 .

EXAMPLE 8

The following solutions are employed:

Solution I: A hydrochloric acid- TiCl_4 solution containing 10% TiCl_4 , 5% HCl and 10 g. $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ per liter;

Solution II: A hydrochloric acid-tin (II) solution containing 200 g. $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, 50 g. HCl and 50 g. $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ per liter; and

Solution III: A KClO_3 solution containing 40 g. KClO_3 per liter.

60 g. of muscovite with a diameter of about 10 to 40 μ are suspended in completely deionized water and the suspension is adjusted with Solution I to a pH value of 2.0. After heating to 75° C., 40 ml. of Solution I are slowly added simultaneously with a 15% aqueous sodium hydroxide solution so as to keep the pH value at a constant 2.0. About 15 minutes after addition is complete, 60 ml. of Solution II is added slowly simultaneously with 60 ml. of Solution III and with 15% aqueous sodium hydroxide solution at a rate which keeps the pH value at a constant 2.0. About 30 minutes after the addition of the tin solution is complete, in order to permit the hydrolysis to go to completion, the coating operation is continued in the same manner according to the following scheme, alternately employing titanium tetrachloride and tin chloride solutions, at a constant pH 2:

Oxide Layer Produced	Solution I	Solution II	Solution III
TiO ₂	320 ml.	—	—
SnO ₂	—	60 ml.	60 ml.
TiO ₂	320 ml.	—	—
SnO ₂	—	60 ml.	60 ml.
TiO ₂	320 ml.	—	—
SnO ₂	—	60 ml.	60 ml.
TiO ₂	320 ml.	—	—
SnO ₂	—	60 ml.	60 ml.

The product is worked up as in Example 1 and calcined at 900° C. for 40 minutes. The pigment exhibits a strong green interference color with good gloss. Roentgenographic investigation reveals the TiO₂ is solely in rutile form.

The pigment contains 40% mica, 35% rutile, 21% SnO₂ and about 3% Al₂O₃ (determined by back titration).

The preceding examples can be repeated with similar success by substituting the generically or specifically described reactants and/or operating conditions of this invention for those used in the preceding examples.

From the foregoing description, one skilled in the art can easily ascertain the essential characteristics of this invention and, without departing from the spirit and scope thereof, can make various changes and modifications of the invention to adapt it to various usages and conditions.

What is claimed is:

1. In a lustrous mica flake pigment wherein the mica flakes are coated with a plurality of metal oxide layers consisting essentially of alternating layers of TiO₂ and SnO₂ in which each rutile layer is roentgenographically free from the anatase form, the improvement wherein the metal oxide layers comprise the sequence rutile/SnO₂/rutile and the innermost layer is rutile and wherein the thickness of the innermost rutile layer is a maximum of about 25 nm.

2. A pigment according to claim 1 wherein the outermost metal oxide layer is rutile.

3. A pigment according to claim 1 wherein the collective SnO₂ content of the metal oxide layers is 13.1 to 37.5 wt. %.

4. A pigment according to claim 1 wherein at least one of the rutile/SnO₂/rutile layers contains Al₂O₃ in a collective amount sufficient to prevent crack formation when tin dioxide hydrate layers of high water content are calcined and to promote the formation of smooth tin dioxide layers and the quantitative deposition of the precipitates on the mica surface.

5. A pigment according to claim 4 wherein each layer contains aluminium oxide, in an amount collectively of up to 10 wt. %.

6. A pigment according to claim 1 wherein the SnO₂ content of the pigment is about 3 to 25 wt. %.

7. A pigment according to claim 1 wherein the rutile content of the pigment is about 7 to 70 wt. %.

8. A mica flake pigment according to claim 1 wherein the metal oxide coating consists of three layers wherein the innermost layer consists of rutile, the middle layer consists of SnO₂ and the outermost metal oxide layer consists of rutile, wherein the SnO₂ content of the pigment is about 3 to 25 wt. % and of the metal oxides is about 13.1 to 37.5 wt. % and the rutile content of the pigment is about 7 to 70 wt. % and of the metal oxides is about 86.9 to about 62.5 wt. %.

9. A mica flake pigment according to claim 1 wherein the collective SnO₂ content of the metal oxide layers is at least 5 wt. %, wherein the SnO₂ layer contains aluminium oxide in an amount of up to 10 wt. % and wherein the outermost metal oxide layer is rutile of a thickness of at least 20 nm.

10. In a process for the production of a TiO₂ coated mica flake pigment comprising a layer on the mica flakes of TiO₂ in the rutile form only over a layer of SnO₂, wherein tin hydroxide and titanium hydroxide are precipitated successively onto the mica flakes from a tin salt solution and a titanium salt solution, respectively, and the thus-coated flakes are then washed, dried and calcined, the improvement which comprises coating the mica flakes first with a thin layer of titanium hydroxide of up to 25 nm. thickness; precipitating the layer of tin hydroxide onto the thus-coated mica flakes from a tin II salt solution; in the presence of an oxidizing agent and then depositing a further layer of titanium hydroxide onto the coated mica flakes.

11. A process according to claim 10 wherein the tin hydroxide is precipitated in the presence of KClO₃ as the oxidation agent.

12. A process according to claim 10 wherein at least tin hydroxide layer is formed in the presence of a water-soluble aluminium salt.

13. A process according to claim 10 wherein the titanium and tin hydroxide layers are formed successively without isolation of the intermediate products.

14. A process according to claim 10 wherein the final metal oxide layer deposited on the mica flakes is titanium hydroxide.

15. A process according to claim 10 wherein at least the tin hydroxide layer is formed in the presence of a water-soluble aluminum salt, and wherein the titanium and tin hydroxide layers are formed successively without isolation of the intermediate products.

16. A process according to claim 15 wherein the tin hydroxide is precipitated in the presence of KClO₃ as the oxidation agent.

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United States Patent [19]

Franz et al.

[11] Patent Number: 4,744,832

[45] Date of Patent: May 17, 1988

[54] IRON OXIDE COATED PEARLESCENT PIGMENTS

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[21] Appl. No.: 894,138

[22] Filed: Aug. 7, 1986

[30] Foreign Application Priority Data

Aug. 7, 1985 [DE] Fed. Rep. of Germany 3528256

[51] Int. Cl.⁴ C09C 1/24; C09C 1/36

[52] U.S. Cl. 106/309; 106/291; 106/300; 106/304; 106/308 B; 428/324

[58] Field of Search 106/291, 300, 304, 308 B, 106/309; 428/324

[56] References Cited

U.S. PATENT DOCUMENTS

3,087,828 4/1963 Linton 106/291
3,553,001 1/1971 Kohlschutter .
3,711,308 1/1973 Brand et al. 106/308 B

3,874,890 4/1975 Bernhard et al. 106/291
3,926,659 12/1975 Bernhard et al. 106/291
4,086,100 4/1978 Esselborn et al. 106/291
4,146,403 3/1979 Armanini et al. 106/291
4,499,143 2/1985 Panush 106/291
4,551,491 11/1985 Panush 106/304
4,552,593 11/1985 Ostertag 106/291
4,615,940 10/1986 Panush et al. 428/324

FOREIGN PATENT DOCUMENTS

208578 8/1979 Czechoslovakia .
2009566 6/1972 Fed. Rep. of Germany .
1359933 7/1974 United Kingdom .

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[57] ABSTRACT

The application relates to a pearlescent pigments based on platelet-like substrates, such as mica, which are coated with metal oxides, the metal oxide layer containing titanium and also iron, wherein the pigment has a multi-layer structure in which a first layer of TiO₂ in the rutile form is followed by a layer of pseudobrookite and an iron oxide layer.

16 Claims, No Drawings

IRON OXIDE COATED PERLESCENT PIGMENTS BACKGROUND OF THE INVENTION

The invention relates to pearlescent pigments based on platelet-like substrates, e.g., mica, which are coated with metal oxides, the metal oxide layer containing both titanium and iron.

Iron-containing mica flake pigments have already been described in the art and have also been used successfully for many years. The pigments described include not only pigments in which iron oxide is precipitated onto the mica platelets together with another metal oxide, in particular titanium dioxide, but also pigments in which the precipitations are carried out in succession.

U.S. Pat. No. 3,087,828 describes obtaining, by means of precipitation of an Fe_2O_3 layer onto a TiO_2 layer, golden-colored pigments which take on a reddish hue after calcination. German Pat. No. 1,959,998, corresponding to U.S. Pat. No. 3,711,308, describes pigments which possess on mica an initial mixed layer of titanium oxide and iron oxide and thereon a top layer of titanium and/or zirconium dioxide.

German Pat. No. 2,244,298, corresponding to U.S. Pat. No. 3,874,890, describes a process for preparing golden-colored pearlescent pigments in which a TiO_2 - and/or ZrO_2 -coated mica pigment is first coated with iron(II) hydroxide, which is then oxidized to Fe_2O_3 .

German Offenlegungsschrift No. 2,313,331, corresponding to U.S. Pat. No. 3,926,659, describes advantageous iron-containing pigments in which the iron oxide is present in certain defined crystal modifications.

Also, German Offenlegungsschrift No. 2,723,871, corresponding to U.S. Pat. No. 4,146,403, describes mica pigments which have a thick Fe_2O_3 layer on a very thin TiO_2 or Al_2O_3 layer.

In all the cases described, TiO_2 is applied in the anatase form. However, on calcination of the pigment the precipitated iron oxide diffuses very strongly into the TiO_2 layer, so that even in those cases where initially separate layers of TiO_2 and Fe_2O_3 are precipitated, a mixed layer consisting essentially of pseudobrookite is present after the calcination.

German Pat. No. 2,522,572, corresponding to U.S. Pat. No. 4,086,100, has proposed providing mica pigments coated with TiO_2 in the rutile form with an additional top layer of coloring metal oxides, among which Fe_2O_3 is mentioned. With relatively low amounts of iron oxide in these coatings, it has been observed that on calcination the iron oxide diffuses to form a mixed layer of pseudobrookite on the rutile base.

By "a relatively low amount of iron oxide" is meant a content of iron oxide which is not substantially greater than about 5% by weight based on the total pigment weight.

SUMMARY OF THE INVENTION

It has now been found, surprisingly, that rutile and anatase differ substantially as relates to the diffusion of iron oxide during calcination. While in the case of anatase even large amounts of iron oxide will virtually completely diffuse into the TiO_2 layer during calcination to form pseudobrookite, it has been found that in the case of a rutile layer, the rate of diffusion is so low that only a relatively thin pseudobrookite layer forms

on the rutile layer, while the remainder of the precipitated iron oxide is actually present in the form of Fe_2O_3 .

Indeed, in the case of the new pigments, which are distinctly improved as regards luster and stability, it is possible, in contrast to the prior art pigments where the iron oxide layer is precipitated onto an anatase layer, to use X-ray diffraction to detect adjacent discrete phases of rutile TiO_2 and of Fe_2O_3 .

Surprisingly, pigments having such a 3-layer structure possess not only distinctly improved color characteristics (improved tinctorial strength and brilliance and improved hiding power) but also an improved chemical stability for example, with respect to photoactivity or as smelting fluxes for glazings and enamel.

The invention, therefore, provides in pearlescent pigments based on platelet-like substrates, especially mica substrates, which are coated with metal oxides, the metal oxide layer containing titanium and also iron, the improvement wherein the pigment has a multilayer structure in which a first layer of TiO_2 in the rutile form is covered with a layer of pseudobrookite which in turn, is covered by an iron oxide layer.

The invention, in a process aspect, involves a process for preparing pearlescent pigments by coating platelet-like substrates such as mica with an iron- and titanium-containing metal oxide layer, the improvement wherein first a titanium dioxide or titanium dioxide hydrate layer is precipitated thereon, the precipitation being effected in a manner known wherein a rutile layer is formed on calcination, and in that either before or after calcination of this pigment an iron oxide or hydroxide layer is precipitated thereon. The pigment is thereafter calcined.

DETAILED DESCRIPTION

It is critical in the present invention that the TiO_2 layer is applied in such a way that the rutile structure is formed on calcination. This can be effected, e.g., by one of the known methods, in which foreign ions, in particular tin (IV), are incorporated into the layer. These methods are described, e.g., in German Pat. No. 2,214,545 and the aforementioned U.S. Pat. No. 4,086,100, utilization being forced by incorporating tin dioxide close to the mica or in discrete layers between the TiO_2 . However, there are other known methods, such as, for example, the incorporation of zinc oxide in accordance with Czech Pat. No. 208,578 or the incorporation of iron(III) into the TiO_2 layer in accordance with German Pat. No. 1,959,998, corresponding to U.S. Pat. No. 3,711,308, which also lead to rutile layers which can be utilized within the context of the present invention.

There are essentially two known processes for precipitating the TiO_2 layer. In one, the precipitation can be effected as described in U.S. Pat. No. 3,087,828 by addition of a sulfuric acid titanyl sulfate solution to the mica suspension and hydrolysis thereof by heating to about 100°C ., the layer thickness and the associated interference color being initially predetermined by the amount of titanyl sulfate present. However, the precipitation can also be carried out as described in German Pat. No. 2,009,566, wherein an aqueous titanium salt solution is gradually added to a hot mica suspension at about $50^\circ\text{--}100^\circ\text{C}$., preferably $70^\circ\text{--}80^\circ\text{C}$., and by the simultaneous addition of a suitable base, for example, an aqueous ammonia solution of an aqueous alkali metal hydroxide solution, a substantially constant pH value of about 0.5-5, in particular, about 1.5-2.5, being maintained. As soon as the desired layer thickness of the

TiO₂ precipitate is reached, the addition of the titanium salt solution is stopped.

To obtain the titanium dioxide layer in the desired rutile structure, the precipitation is modified in the known manner so that either a tin salt is present in the mica suspension and is hydrolyzed together with the titanyl sulphate, or that after the precipitation of a thin TiO₂ layer, an SnO₂ intermediate layer and then an additional TiO₂ layer are precipitated thereon, it being possible to repeat these alternating precipitations several times, as required.

The iron oxide layer can also be precipitated thereon by known methods. In this aspect it is possible to start not only from iron(III) salts, as described, for example, in German Pat. No. 1,467,468, but also from iron(II) salts, as described in U.S. Pat. No. 3,874,890; the initially formed coating of iron(II) hydroxide is oxidized to iron(III) oxide hydrate.

Precipitation of the iron oxide layer can be effected not only onto a calcined and, hence, already rutilized TiO₂ layer, but also directly after the TiO₂ precipitation onto the uncalcined pigment. In the latter case, the subsequent calcination is surprisingly accompanied by a very low diffusion of the iron into the TiO₂ layer, although relatively high temperatures of about 700° to about 950° C., preferably about 800° to about 900° C., are used in the calcination, and the conventional calcination times of about 10 to 200, preferably 20 to 100, minutes are used.

Since even when utilizing the rutile TiO₂ substrate taught herein, a small amount of diffusion of iron oxide into the TiO₂ layer with an accompanying formation of pseudobrookite cannot be completely avoided, the TiO₂ layer should have a certain minimum thickness of about 40 nm, so as to produce a 3-layer structure of TiO₂/pseudobrookite/Fe₂O₃. In general, the layer thicknesses of the TiO₂ layer before calcination range from about 40 to about 200 nm and preferably, thicknesses of about 40 to about 150 nm are preferred. It is also preferred that the titanium content, calculated as TiO₂, relative to the total pigment is about 20-50% by weight.

An essential feature of the 3-layer structure taught herein is the particular layer thickness of the precipitated Fe₂O₃. This thickness should always be sufficiently large so that after the calcination and the resulting formation of an intermediate layer of pseudobrookite a pure Fe₂O₃ layer still remains on the surface of the pigment particles. For that reason the Fe₂O₃ layer precipitated is at least about 15 nm thick and preferably has a thickness of about 15 to about 50 nm, most preferably about 20 to about 40 nm. The iron content calculated as Fe₂O₃, relative to the total pigment as a rule is about 10-50% by weight. Iron oxide contents of at least 15% by weight are preferred.

It is also possible to incorporate a variety of dopants, in particular other colored or colorless metal oxides, not only into the TiO₂, but also into the Fe₂O₃ layer. Suitable dopants include compounds of aluminum(III), silicon(IV), zirconium(IV), chromium(III), boron(III) and phosphorus(V). These dopants are each incorporated, where appropriate, in amounts of about 0 to 2% by weight. However, total amounts of about 2% in case only one or two dopants are used and in case the dopants are incorporated in the TiO₂ layer, to about 5% by weight in case more than two dopants are used or the dopants are incorporated in the iron oxide layer, should not be exceeded. Larger amounts of dopants are on the

one hand not necessary and show on the other hand a tendency to influence negatively the quality of the pigments.

If dopants are to be incorporated in one or even all of the layers, they can be added either to the mica suspension, to one of the added salt solutions, or where appropriate, to the added base in the form of water-soluble salts. The dopants are generally homogeneously distributed in the metal oxide layer(s). However, it is also possible and may be advantageous to effect such an enrichment either close to the mica or at the surface of the pigment.

It is also possible to subject the pigment to a subsequent coating or treatment which further increases its light, weather or chemical stability or facilitates the handling of the pigment, particularly regarding the incorporation of it into various media. Representative aftercoatings or aftertreatments include the methods described in German Pat. No. 2,215,191, German Offenlegungsschrift Nos. 3,151,354, 3,235,017 and 3,334,598. Owing to the fact that even without these additional measures the pigments fabricated according to the teachings of the invention have excellent properties, these optionally applied substances only account for about 0 to 5, and preferably about 0 to 3% by weight of the total pigment.

The pigments of the invention can be used like the hitherto disclosed pigments; for example, for pigmenting plastics, inks, paints, body care agents and cosmetics, as well as owing to their high chemical stability they also can be used in smelting fluxes for glazes and enamel.

Without further elaboration, it is believed that one skilled in the art can, using the preceding description, utilize the present invention to its fullest extent. The following preferred specific embodiments are, therefore, to be construed as merely illustrative, and not limitative of the remainder of the disclosure in any way whatsoever.

In the preceding text and the following examples, all temperatures are set forth uncorrected in degrees Celsius and all parts and percentages are by weight; unless otherwise indicated.

EXAMPLE 1

In accordance with Example 1A of German Pat. No. 2,214,545, 100 g of mica are coated in succession with 0.8 g of SnO₂ and 30 g of TiO₂ in aqueous suspension. The suspended uncalcined pigment exhibits a slightly yellow interference color. After switching off the stirrer and allowing the pigment to settle out, the supernatant liquor is drawn off, the 2500 ml of water, 81 g of anhydrous FeCl₃ and 16 g of sodium acetate are added. One hour of heating at 70°-80° C. is followed by filtration, washing until chloride-free, drying, and calcination at 850° C. for 30 min. The result obtained is a pigment having a very dark golden pigment and interference color, the X-ray diffraction values of which (Debye-Scherrer diagram) reveal that discrete layers of rutile, pseudobrookite and haematite are present on the muscovite.

The pigment is very stable in glazes and exhibits no photoactivity in the Kronos test.

COMPARATIVE EXAMPLE 1A

Example 1 is repeated, except without the SnO₂ precipitation. The result obtained is a pigment with a bright yellow pigment and yellow interference color, the coat-

ing of which consists of anatase and pseudobrookite, according to the X-ray diffraction values. The stability of the pigment in glazes is poor, and in the Kronos test it exhibits photoactivity.

EXAMPLE 2

In accordance with Example 2 of German Pat. No. 2,522,572, corresponding to U.S. Pat. No. 4,086,100, 109 g of a pigment having a blue interference color are prepared by alternately coating mica with TiO_2 , SnO_2 and TiO_2 . The settling out of the pigment is followed by decanting and addition of 2500 ml of water. To the suspension which has been heated to 75° C. and brought to a pH 6-7 with ammonia being gradually added, while air is blown in at the same time, a solution of 120 g of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ in 400 ml of water and 1.5 ml of concentrated sulphuric acid is added, with the pH value being largely maintained constant by simultaneous addition of ammonia. The pigment is then separated off, washed until sulphate-free and dried and calcined at 850° C. for 30 min. The result obtained is a golden, lustrous pigment having a green interference color, and high hiding power, which, on the basis of the X-ray diffraction values, possesses layers of rutile, pseudobrookite and haematite. It exhibits high stability in glazes and no photoactivity in the Kronos test.

COMPARATIVE EXAMPLE 2A

Example 2 is repeated, except that the SnO_2 intermediate layer is left out. The result obtained is a pigment having a bright yellow pigment and green interference color, which according to the X-ray diffraction values carries a coating of anatase and pseudobrookite. It exhibits poor stability in glazes and photoactivity in the Kronos test.

EXAMPLE 3

In accordance with the process of Example 1 of German Pat. No. 1,959,998, a mixed precipitate of hydrated titanium dioxide and hydrogenated iron(III) oxide is applied to 100 g of mica in aqueous suspension. As soon as an orange-colored interference is obtained, the pigment is allowed to settle out, the supernatant liquor is decanted off, and water is added to bring the volume to 2500 ml. Thereafter iron oxide is precipitated, on as described in Example 2, again using 120 g of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$. Working up and calcination as in Example 2 gives a copper-colored pigment with a blue interference color and high stability, which shows rutile, pseudobrookite and haematite in the X-ray diffraction diagram. It possesses high stability in glazes and no photoactivity in the Kronos test.

The preceding examples can be repeated with similar success by substituting the generically or specifically described reactants and/or operating conditions of this invention for those used in the preceding examples.

From the foregoing description, one skilled in the art can easily ascertain the essential characteristics of this invention, and without departing from the spirit and scope thereof, can make various changes and modifications of the invention to adapt it to various usages and conditions.

What is claimed is:

1. In a pearlescent pigment comprising a plateletlike substrate coated with metal oxides, the metal oxide layer containing titanium dioxide and iron oxide, the improvement wherein the pigment comprises a multi-layer structure in which superimposed on the substrate

is a first layer of TiO_2 in the rutile form, formed from a precipitated layer of titanium dioxide or titanium dioxide hydrate, having a thickness of at least 40 nm, the latter being superimposed by a layer of pseudobrookite and the latter being superimposed by an iron oxide layer, formed by the precipitation of an iron oxide or hydroxide layer, having a thickness of at least 15 nm, wherein the TiO_2 concentration, relative to the total pigment, is about 20 to about 50% by weight, and the iron oxide concentration relative to the total pigment, is about 10 to about 50% by weight.

2. A pearlescent pigment according to claim 1, wherein the substrate is mica.

3. A pearlescent pigment according to claim 1, wherein dopants which are selected from compounds of aluminum(III), silicon(IV), zirconium(IV), chromium(III), boron(III) and phosphorous(V) are incorporated into at least one of the TiO_2 and Fe_2O_3 layers, said copants being present in a total of not more than about 5% by weight based on the pigment.

4. In a process for preparing pearlescent pigments by coating platelet-like substrates with an iron- and titanium-containing metal oxide layer, the improvement comprising first precipitating a titanium dioxide or titanium dioxide hydrate layer having a thickness of at least 40 nm and a concentration relative to the total pigment of about 20-50% by weight, said layer being calcinable to form a rutile layer, and before or after calcination of resultant pigment, precipitating an iron oxide or hydroxide layer having a thickness of at least 15 nm, and a concentration relative to the total pigment of about 10-50% by weight on the titanium dioxide or the titanium dioxide hydrate layer, and calcining the pigment.

5. A process according to claim 4, the step of precipitating said layer calcinable to rutile comprises precipitation of a TiO_2 layer, an SnO_2 intermediate layer and then an additional TiO_2 layer onto the platelet-like substrate.

6. A process according to claim 4, wherein the calcination occurs at about 700° to 950° C.

7. A process according to claim 4, wherein the TiO_2 layer is about 40 to about 200 nm.

8. A process according to claim 4, wherein the TiO_2 layer is about 40 to about 200 nm.

9. A process according to claim 8, wherein the iron oxide layer has a thickness of about 20 to 40 nm.

10. A process according to claim 4, wherein the iron oxide is precipitated onto an uncalcined titanium dioxide or titanium dioxide hydrate layer.

11. A process according to claim 4, wherein the titanium dioxide or titanium dioxide hydrate layer has a thickness of about 40-150 nm.

12. A process according to claim 4, wherein the iron oxide is Fe_2O_3 and the Fe_2O_3 layer has a thickness of about 15-50 nm.

13. A process according to claim 12, wherein the Fe_2O_3 layer has a thickness of about 20-40 nm.

14. A pearlescent pigment according to claim 1, wherein the iron oxide concentration, relative to the total pigment, is 15-50% by weight.

15. A process according to claim 4, wherein the iron oxide concentration, relative to the total pigment, is 10-50% by weight.

16. A process according to claim 4, wherein the iron oxide concentration, relative to the total pigment, is about 15-50% by weight.

* * * * *

United States Patent [19]

Ambrosius et al.

[11] Patent Number: 4,867,794

[45] Date of Patent: Sep. 19, 1989

[54] PROCESS FOR PREPARING
RUTILE-COATED MICA PIGMENTS

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[21] Appl. No.: 131,605

[22] Filed: Dec. 11, 1987

[30] Foreign Application Priority Data

Dec. 13, 1986 [DE] Fed. Rep. of Germany 3642647

[51] Int. Cl.⁴ C04B 14/20; C07C 3/06

[52] U.S. Cl. 106/417; 166/415;
166/441

[58] Field of Search 106/291, 300, 308 B,
106/309, 415, 417, 441, 436

[56] References Cited

U.S. PATENT DOCUMENTS

3,553,001	1/1971	Kohlschutter et al.	
4,038,099	7/1977	DeLuca, Jr. et al.	106/291
4,040,859	8/1977	Esselborn et al.	106/291
4,086,100	4/1978	Esselborn et al.	106/291

Primary Examiner—Paul Lieberman

Assistant Examiner—Christine A. Skane

Attorney, Agent, or Firm—Millen, White & Zelano

[57] ABSTRACT

In mica/titanium dioxide pigments reliable rutilization is obtained with small amounts of tin by precipitating tin dioxide directly on the mica and completing this precipitation before the precipitation of titanium dioxide is started.

9 Claims, No Drawings

PROCESS FOR PREPARING RUTILE-COATED MICA PIGMENTS

BACKGROUND OF THE INVENTION

The invention relates to a process for preparing pearl luster pigments based on metal oxide coated mica flakes wherein, to coat with titanium dioxide in the rutile form, not only TiO_2 but also SnO_2 is precipitated onto the mica flakes in aqueous suspension and the pigment is then washed, dried and calcined.

Processes for preparing rutile-containing mica pigments are known not only from German Patent Specifications Nos. 2,214,545 and 2,522,572 (equivalent to U.S. Pat. No. 4,086,100) but also from U.S. Pat. No. 4,038,099.

In the process of DE Patent No. 2,522,572, first a very thin titanium dioxide layer is precipitated onto mica flakes followed alternately by at least one SnO_2 and TiO_2 layer, thicker layers being prepared by alternately precipitating a plurality of SnO_2 and TiO_2 layers. These SnO_2 and TiO_2 layers are in each case prepared by slowly adding to the mica suspension, together with a base for keeping the pH constant, the tin salt solution with or without an oxidizing agent in the one case and the titanium salt solution in the other. In this way the precipitation can be very simply continued until the metal oxides are present in the desired layer thickness and consequently the pigment has the desired interference color. Customary washing, drying and calcining produces very brilliant pigments. However, a disadvantage is the very complicated process, in particular in the case of relatively thick layers. In addition, it requires relatively high tin dioxide contents, which in general range from about 5 to 7% by weight, based on the completed pigment.

It is true that the process of DE Patent 2,214,545 and U.S. Pat. No. 4,038,099 can be carried out with smaller amounts of tin, but other serious disadvantages remain. In this process, the mica suspension has added to it the solution of a tin salt and then a strong acid, and a portion of the tin precipitates as water-containing tin oxide on the mica flakes. Thereafter a titanyle sulfate solution is added, and the suspension is heated to a boil; as a result of hydrolysis and precipitation, titanium dioxide deposits on the mica flakes and, in the course of this process, the remaining tin is incorporated as a tin oxide in the titanium dioxide layer as it forms.

In this hydrolysis process, the thickness of the metal oxide layer and hence the interference color of the pigment is determined from the start by the amount of metal salt added. Corrections in the course of the coating process and in particular accurate end point determination as in the process of DE Patent No. 2,522,572 are not possible.

However, it has been found, surprisingly, that it is not even possible to combine the tin dioxide precipitation as described in DE Patent No. 2,214,545 with the titanium dioxide precipitation as described in DE Patent No. 2,522,572. Evidently, the tin salt remaining in solution interferes with the titanium dioxide precipitation to such an extent as to produce only qualitatively very poor pigments whose rutile content is a non-reproducible 100%.

SUMMARY OF THE INVENTION

It is therefore an object of the present invention to find a process by means of which a titanium dioxide

coating can be reliably deposited in the rutile modification on mica platelets, which is very simple to carry out in industry, in which the titanium dioxide coating can be effected by simultaneously metering in titanium salt and base, and in which the tin content can be restricted to values below 1% by weight.

Upon further study of the specification and appended claims, further objects and advantages of this invention will become apparent to those skilled in the art.

It has now been found that these objects can be achieved if first a homogeneous coating of the mica with tin dioxide is carried out in such a way that ideally no tin salt remains in solution and only then the titanium dioxide layer is precipitated.

The present invention accordingly provides a process for preparing pearl luster pigments based on metal oxide coated mica flakes wherein, to coat with titanium dioxide in the rutile form not only titanium dioxide but also tin dioxide is precipitated from aqueous metal salt solutions onto the mica flakes in aqueous suspension and the pigment is then washed, dried and calcined, which is characterized in that the precipitation of the tin dioxide is concluded before the addition of the titanium salt solution.

DETAILED DESCRIPTION

Surprisingly, this process gives a 100% rutilization in a very reliable manner even in the case of thick titanium dioxide layers even though only small amounts of tin need to be used. For instance, even an amount of about 0.25% by weight is sufficient. It is only to be on the safe side that in general a somewhat higher tin content of about 1% is preferred. However, these values are based on the weight of the mica used, so that the values based on the end product are still appreciably lower, depending on the amount of titanium dioxide precipitated on. It is also surprising that the amount of tin dioxide required for the process of rutilization is substantially independent of the particle size of the mica used.

To precipitate the tin dioxide, the mica suspension is brought to a suitable pH. In general, a suitable pH range is from about 0.5 to 3, in particular from about 1.0 to 2.5. For the purposes of the present invention, the range from about 1.5 to 2.0 has been found to be particularly advantageous. Thereafter the tin salt solution is metered in together with a base, preferably at a temperature of about 50° C. to about 100° C.

The tin salt used can in principle be any available divalent or tetravalent tin salt. On account of the easy accessibility and the low cost, it is preferable to use SnCl_4 , the pentahydrate producing particularly good coatings. The base with which the pH of the suspension is maintained substantially constant during the coating step is freely choosable in principle, so that for example alkali metal hydroxide solutions, in particular diluted sodium hydroxide solution, ammonium hydroxide or gaseous NH_3 or, if desired, even conventional buffer systems can be used, the contents of which can be easily determined by one of ordinary skill in the art.

Other parameters of the tin dioxide precipitation, e.g. time, temperature and concentration of solutions, are wholly conventional as disclosed in U.S. Pat. No. 4,040,859. By following the above mentioned process parameters a substantially complete precipitation of tin dioxide is reached, substantially complete meaning that only such minor amounts of tin salts remain in solution

which don't negatively influence the following precipitation of titanium dioxide.

After the precipitation of tin dioxide has ended, the mixture is generally stirred for some minutes to ensure that all the tin has been precipitated, and then the process of titanium dioxide precipitation is started. This process is in principle carried out essentially conventionally, except as noted below, in the manner described in DE Patent No. 2,009,566, where a titanium salt, in particular TiCl_4 , is metered together with a base into the mica suspension at elevated temperatures. Surprisingly, however, it has been found that reliable rutile formation is easily achievable if the pH during the precipitation is not substantially above 2.0. Preferred pH values which are within the same range as in the tin dioxide precipitation process, namely about 1.5 to 2.0.

The coated mica pigments are then worked up in a conventional manner in that the pigment is separated off, washed, dried and then calcined. It has been found to be an advantage with the novel process that 100% rutilization is obtainable even under relatively mild calcination conditions. For instance, an approximately 30-minute calcination at about 850°C . or an equivalent time/temperature combination is sufficient. Compared with the prior art processes, where a time/temperature combination of 30 minutes/ 950°C . is customary, this further serves to keep the process simple and economical. Suitable equivalent time/temperature combinations may be determined conventionally according to known principles.

It has already been mentioned that using the process according to the invention even thick titanium dioxide layers can be reliably obtained in the rutile form without incorporation of tin dioxide in the layer or as an intermediate layer. In the Examples below, this is illustrated by reference to pigments having a green interference color, since they have a particularly thick titanium dioxide layer. However, since the titanium dioxide precipitation process can be stopped according to conventional processes at any desired color end point and at any desired layer thickness, the process described makes it possible to prepare any desired pigment with TiO_2 -layers of a thickness of up to 200 nm being reliably in the rutile modification. As a rule the pigments possess diameters of 1–200 μm and thicknesses of about 0.1–5 μm , diameters of about 5–60 μm and thicknesses of about 0.5 μm being preferred, and can be used in all conventional applications.

Without further elaboration, it is believed that one skilled in the art can, using the preceding description, utilize the present invention to its fullest extent. The following preferred specific embodiments are, therefore, to be construed as merely illustrative, and not limitative of the remainder of the disclosure in any way whatsoever.

In the foregoing and in the following examples, all temperatures are set forth uncorrected in degrees Celsius and unless otherwise indicated, all parts and percentages are by weight.

The entire text of all applications, patents and publications, if any, cited above and below are hereby incorporated by reference.

EXAMPLES

EXAMPLE 1

To a suspension of 100 g of mica of a particle size of 10 to 50 μm in 2 l of water are added at 75°C . in the course of one hour 60 ml of an aqueous solution of 3 g

of $\text{SnCl}_4 \times 5\text{H}_2\text{O}$ and 10 ml of concentrated hydrochloric acid while a pH of 1.8 is maintained by the simultaneous addition of dilute sodium hydroxide solution.

An aqueous, approximately 20% strength by weight TiCl_4 solution is then added at a rate of about 2 ml/min while a pH of 1.6 is maintained with dilute sodium hydroxide solution. After a green interference color has been obtained, stirring is continued for approximately a further half hour, and the pigment is separated off, washed with water until salt-free, dried and calcined at 850°C . for 30 minutes. X-ray structure analysis shows that the titanium dioxide layer is 100% in the rutile form.

EXAMPLES 2 to 4

Example 1 is repeated, except that the titanium dioxide precipitation process is carried out at pH 1.8, pH 2.0 and pH 2.2 respectively. X-ray structure analysis shows that 100% rutilization is obtained.

EXAMPLES 5 to 7

Example 1 is repeated, except that the temperature of the suspension is 90°C . and the titanium dioxide precipitation process is carried out at pH 1.6, pH 1.8 and pH 2.0 respectively. X-ray structure analysis shows that 100% rutilization is obtained.

The pigments of Examples 1–7 have a composition conforming to 39.5% by weight of mica, 60.0% by weight of TiO_2 and 0.5% by weight of SnO_2 .

EXAMPLE 8

Example 1 is repeated, except that the amount of tin salt is reduced to 1.5 g of $\text{SnCl}_4 \times 5\text{H}_2\text{O}$. The result obtained is a pigment of composition of 39.6% by weight of mica, 60.1% by weight of TiO_2 and 0.25% by weight of SnO_2 . X-ray analysis shows that 100% rutilization is obtained.

What is claimed is:

1. A process for the preparation of metal oxide coated mica flake pearl luster pigments, comprising precipitating onto a mica flake in aqueous suspension a layer of tin dioxide and a layer of titanium dioxide, wherein the precipitation of the tin dioxide is substantially concluded before the precipitation of the titanium dioxide is begun.
2. A process according to claim 1, wherein the tin dioxide is precipitated from an aqueous solution of a divalent or tetravalent tin salt and the titanium dioxide is precipitated from an aqueous solution of TiCl_4 .
3. A process according to claim 2, wherein the tin salt is SnCl_4 .
4. A process according to claim 3, wherein the tin salt is $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$.
5. A process according to claim 1, wherein the tin salt is used in such an amount that the tin content of the pigment, based on the mica used, is about 0.25 to 1.0% by weight.
6. A process according to claim 1, wherein the tin dioxide is precipitated at a pH of about 1.5 to 2.0.
7. A process according to claim 6, wherein the titanium dioxide is precipitated at a pH of about 1.5 to 2.0.
8. A process according to claim 1, wherein the precipitation of the metal oxides is carried out at a temperature of about 50° to about 100°C .
9. A process according to claim 1, wherein the pigment is calcined at about 850°C . for at least thirty minutes or under conditions equivalent thereto.

UNITED STATES PATENT AND TRADEMARK OFFICE
CERTIFICATE OF CORRECTION

PATENT NO. : 4,867,794

DATED : September 19, 1989

INVENTOR(S) : KLAUS AMBROSIUS ET AL

It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

Column 4, claim 1, line 45:

reads "begun."

should read -- begun and is effected by adding a tin salt solution to an aqueous mica suspension at elevated temperature while simultaneously adding a base, so as to maintain a pH at which the tin is quantitatively precipitated as tin dioxide or tin dioxide hydrate on the mica.

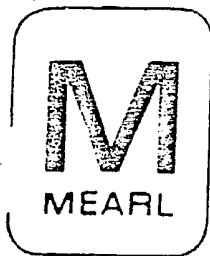
Signed and Sealed this
Fourth Day of September, 1990

Attest:

HARRY F. MANBECK, JR.

Attesting Officer

Commissioner of Patents and Trademarks



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PRODUCT SPECIFICATIONS & PROPERTIES

FLAMENCO TWILIGHT GOLD

Product No. 230ZB

Description:

An greyish, free flowing powder with a pale yellow reflection.

Pigment Type:

Platelets of mica coated with titanium dioxide and iron oxide and a small amount of stannic oxide.

Chemical Composition:

	By Weight	CI No.	CAS No.
Mica	42 - 57%	77019	12001-26-2
TiO ₂	30 - 39%	77891	1317-80-2
Cos. Black Fe ₃ O ₄	13 - 17%	77499	1317-61-9
SnO ₂	0.2 - 2.0%	77861	18282-10-5

CTFA Definition:

Mica and titanium dioxide and iron oxide.

Trace Elements:

Lead (Pb)	15 ppm max.
Arsenic (As)	2 ppm max.

Microorganisms:

100/grams max. No Gram negatives (detection limit <10 org/gram).
No Pathogens.

pH:

7.0 - 11.0 (4% aqueous suspension)

TYPICAL PROPERTIES

Particle Size:

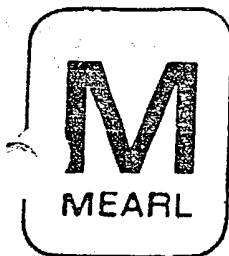
95% of platelets are between 6 - 48 μ m in length by light scattering measurement on the 230Z.

Density:

3.4 Kg/L 27.9 lbs/gal

Bulk Density (Appx.):
(ASTM D-716-86)

24 g/100 cm³ 3.9 g/in³ Appx. 15 lbs/ft³



The Mearl Corporation

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PRODUCT SPECIFICATIONS & PROPERTIES

CLOISONNE REGAL GOLD

Product No. 233XB

Description:

A greyish gold, free flowing powder.

Pigment Type:

Platelets of mica coated with titanium dioxide and iron oxide and a small amount of stannic oxide.

Chemical Composition:

	By Weight	CI No.	CAS No.
Mica	36 - 51%	77019	12001-26-2
TiO ₂	33 - 40%	77891	1317-80-2
Cos. Black Fe ₃ O ₄	13 - 17%	77499	1317-61-9
Fe ₂ O ₃	3 - 6%	77491	1309-37-1
SnO ₂	0.1 - 1.0%	77861	18282-10-5

CTFA Definition:

Mica (and) Titanium Dioxide (and) Iron Oxide.

Trace Elements:

Lead (Pb) 15 ppm max.
Arsenic (As) 2 ppm max.

Microorganisms:

100/grams max. No Gram negatives (detection limit < 10 org/gram).
No Pathogens.

pH:

6.0 - 10.5 (4% aqueous suspension)

TYPICAL PROPERTIES

Particle Size:

95% of platelets are between 6 - 48 μ m in length by light scattering measurement on the 233X.

Density:

3.45 Kg/L 28.7 lbs/gal

**Bulk Density (Appx.):
(ASTM D-716-86)**

25.6 g/100 cm³ 4.2 g/in³ Appx. 16 lbs/ft³



US005223034A

United States Patent [19]

Nitta et al.

[11] Patent Number: **5,223,034**[45] Date of Patent: * **Jun. 29, 1993**

[54] **WEATHER-RESISTANT, PEARLESCENT PIGMENT AND PROCESS FOR PRODUCING THE SAME IN THE PRESENCE OF HYPOPHOSPHITE**

[75] Inventors: **Katsuhisa Nitta, Fukushima; Isao Suzuki, Funabashi, both of Japan**

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[*] Notice: The portion of the term of this patent subsequent to May 9, 2006 has been disclaimed.

[21] Appl. No.: **696,268**

[22] Filed: **May 1, 1991**

Related U.S. Application Data

[63] Continuation of Ser. No. 353,834, May 18, 1989, abandoned.

[30] Foreign Application Priority Data

May 19, 1988 [JP] Japan 63-120689

[51] Int. Cl.⁵ **C04B 14/20; C04B 14/30**

[52] U.S. Cl. **106/417; 106/450; 106/480**

[58] Field of Search **106/417, 450, 480, 503**

[56] References Cited**U.S. PATENT DOCUMENTS**

3,087,828 4/1963 Linton 106/417
 3,331,699 7/1967 Marshall et al. 106/450
 3,342,617 9/1967 Jackson 106/417
 3,536,520 10/1970 Marshall 106/417
 3,832,208 8/1974 Jackson 106/441
 3,874,890 4/1975 Bernhard et al. 106/439
 3,892,577 7/1975 Sugahara et al. 106/14.12
 3,926,659 12/1975 Bernhard et al. 106/439

4,457,784 7/1984 Bernhard 106/417
 4,482,389 11/1984 Franz et al. 106/417
 4,525,425 6/1985 Church 427/372.2
 4,565,581 1/1986 Bernhard 106/417
 4,828,623 5/1989 Nitta et al. 106/417
 5,022,923 6/1991 Rau et al. 106/417

FOREIGN PATENT DOCUMENTS

0082986 7/1983 European Pat. Off. 106/417
 02628353 12/1977 Fed. Rep. of Germany 106/417
 0023643 1/1961 Japan 106/417
 0162473 12/1980 Japan 106/480
 3043962 2/1988 Japan 106/417

OTHER PUBLICATIONS

Shaw "New Approach to Ceramic Colors" *Ceramic Industry* Apr. 1962 pp. 85-124.

Blumenthal "Zirconium Compounds in Water Repellents . . ." *Industrial and Engineering Chem.* Apr. 1950 pp.640-642.

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[57]

ABSTRACT

The invention relates to a weather-resistant, pearlescent pigment which comprises mica flakes coated with a metal oxide as base material, (a) hydrated zirconium oxide formed by hydrolysis of a zirconyl compound in the presence of a hypophosphite, and (b) a hydrated metal oxide (or oxides) formed by hydrolysis of a water-soluble compound (or compounds) of at least one member selected from the group consisting of cobalt, manganese and cerium, said components (a) and (b) being deposited on the surface of said base material.

12 Claims, No Drawings

WEATHER-RESISTANT, PEARLESCENT PIGMENT AND PROCESS FOR PRODUCING THE SAME IN THE PRESENCE OF HYPOPHOSPHITE

This application is a continuation of application Ser. No. 07/353,834, filed May 18, 1989, abandoned.

BACKGROUND OF THE INVENTION

We formerly succeeded in developing water-resistant pearlescent pigment that can be applied to paint for outdoor use, particularly to paint for exterior coating of cars (Japanese Patent Application No. 276687/1986, equivalent to allowed U.S. application Ser. No. 07/123,474, filed Nov. 20, 1987).

Paint for outdoor use, for example, paint suitable for exterior coating of cars, must be such that the coated film shows no change in appearance when exposed to various weather conditions.

It is known that particles of titanium dioxide, if contained in a coated film, tend to induce oxidative decomposition of the polymer that constitutes the coated film by the action of near ultraviolet rays and moisture, thus leading to chalking. To suppress such an activity of titanium dioxide, many techniques have been proposed and adopted in commercial products, in which titanium dioxide is doped or coated with a chromium, silicon, aluminum, zinc, phosphorus or zirconium compound, either alone or in combination.

Aluminum flake pigment is also used in paint for exterior coating of cars, and it is known that paint of this type also tends to undergo changes in appearance when exposed to various weather conditions. Known methods for evaluating the tolerance of pigment to weather conditions, are outdoor exposure tests and accelerated weathering tests. When the water resistance alone is to be evaluated, coated boards are exposed to an atmosphere of high temperature and humidity (blister box test) or immersed in hot water (hot-water immersion test) to examine the resulting deterioration in gloss and changes in color.

It is generally accepted that such deterioration in gloss and changes in color are a result of light scattering caused by micropores in the coated film, which have been formed by permeation of water or steam to produce minute blisters, followed by evaporation of the water.

Pearlescent pigments comprising metal-oxide-coated mica (mica flakes with their surface coated with a metal oxide, such as titanium oxide, iron oxide and a combination thereof) have been widely employed in notions for daily use, toys, packaging materials and many other uses as colorants for paint, printing ink and plastics, and their application has recently been expanded to outdoor uses, such as exterior coating for cars and construction materials.

However, conventional pearlescent pigments, when submitted to the water resistance tests (blister box and hot-water immersion tests), show deterioration in gloss and changes in color as in the case with aluminum flake pigments, and hence it has been pointed out that some modification is required for pigments of this type to be applied to paint for outdoor use, particularly to paint for exterior coating of cars.

The pigment of the new type in U.S. Ser. No. 07/127,474 shows excellent gloss and water resistance without using any chromium compound, but is still insufficient in resistance to light. Application of this

technique to mica flakes coated with metal oxides including titanium dioxide failed to fully suppress the adverse activity of titanium dioxide as mentioned above; coated film containing the thus-obtained pigment showed unsatisfactory results when subjected to tests involving light irradiation, such as outdoor exposure tests and accelerated weathering tests.

In the automotive industry, there has been an increasing demand for pearlescent gloss finish, and this requires the development of new pearlescent pigments for outdoor paint that contain no chromium compounds and show high gloss and outstanding weatherability.

This invention provides novel, weather-resistant pearlescent pigments that will meet the above-mentioned requirements, and processes for producing the same.

SUMMARY OF THE INVENTION

This invention relates to pearlescent pigments composed of mica flakes coated with a metal oxide as base material, and a second coating comprising hydrated zirconium oxide and a hydrated oxide (or oxides) of at least one metal selected from the group consisting of cobalt, manganese and cerium, and to processes for producing the same.

More particularly, it relates to novel, weather-resistant pearlescent pigment and to processes for producing the same, in which this novel pearlescent pigment comprises mica flakes coated with a metal oxide as base material, (a) hydrated zirconium oxide formed by hydrolysis of a zirconyl compound in the presence of a hypophosphite, and (b) a hydrated metal oxide (or oxides) formed by hydrolysis of a water-soluble compound (or compounds) of at least one member selected from the group consisting of cobalt, manganese and cerium, said components (a) and (b) being deposited on the surface of said base material.

DETAILED DISCLOSURE OF THE INVENTION

We have discovered that a coating comprising hydrated zirconium oxide formed under specific conditions and a hydrated oxide (or oxides) of at least one metal selected from the group consisting of cobalt, manganese and cerium, show sufficiently high weatherability as required of the above-mentioned pearlescent pigment.

Noting that a coating of hydrated zirconium oxide formed under specific conditions alone was insufficient to give satisfactory results in outdoor exposure tests and accelerated weatherability tests, we further continued studies to overcome this difficulty and succeeded in providing the novel, weather-resistant pearlescent pigments of this invention.

The weather-resistant, pearlescent pigments of this invention comprise mica flakes coated with a metal oxide as base material, (a) hydrated zirconium oxide formed by hydrolysis of a zirconyl compound in the presence of a hypophosphite, and (b) a hydrated metal oxide (or oxides) formed by hydrolysis of a water-soluble compound (or compounds) of at least one member selected from the group consisting of cobalt, manganese and cerium, said components (a) and (b) being deposited on the surface of said base material. This new pearlescent pigment, when applied to paint for outdoor use, gives coated film with outstanding weatherability.

The novel, weather-resistant pearlescent pigment of this invention can be produced according to the methods described below.

Mica flakes coated with a metal oxide are used as base material. An aqueous slurry of this base material is treated, at a temperature in the range from 50° C. to its boiling point in the presence of a hypophosphite, with a salt of zirconium that can be hydrolyzed into hydrated zirconium oxide and with a water-soluble compound (or compounds) of at least one member selected from the group consisting of cobalt, manganese and cerium that can be hydrolyzed into the corresponding hydrated metal oxide (or oxides), thereby causing the hydrated metal oxides to deposit on the surface of said base material. In this case, all of the hydrated metal oxides may be formed simultaneously, or part or all of the individual oxides may be formed separately.

The pearlescent base pigment can thus be coated with hydrated zirconium oxide and a hydrated metal oxide (or oxide) of at least one member selected from the group consisting of cobalt, manganese and cerium, with no adverse effect upon its dispersibility, giving new pearlescent pigment which shows outstanding weatherability when applied to paint for outdoor use.

Any type of commonly employed metal-oxide-coated mica flakes may be used as the base material in the manufacturing processes of this invention. As the metal oxide may be mentioned oxides of titanium, iron, tin, chromium and zirconium, and any combinations of these metal oxides. Of these, the oxide of iron may be ferrous oxide, ferric oxide or a mixture thereof. Preferably used are mica flakes coated with rutile titanium dioxide and those coated with iron oxide containing titanium oxide. These are well-known pigments disclosed in U.S. Pat. Nos. 3 553 001, 3 711 308, 3 874 890, 3 926 659, 3,951,679, 4,084,983, 4,086,100 and 4,128,435.

These base pigments, modified by treatment with a compound of silicon, aluminum or zinc for higher stability, may also be used for the purpose of this invention.

Mica flakes generally have a diameter of 2 to 200 μm and a thickness of about 0.1 to 5 μm , but those about 5 to 50 μm in diameter and about 0.2 to 0.9 μm in thickness are preferably used in the processes of this invention.

As examples of the water-soluble zirconium salts capable of forming hydrated zirconium oxide by hydrolysis, there may be mentioned normal salts such as ZrCl_4 , $\text{Zr}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$ and $\text{Zr}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$, and zirconyl salts such as $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$, $\text{ZrO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$, $\text{ZrO} \cdot \text{SO}_4 \cdot 4\text{H}_2\text{O}$ and $\text{ZrO}(\text{CH}_3\text{COO})_2$. Of these, $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ is the most preferred because of the ease of handling and availability.

Illustrative water-soluble hypophosphites include $\text{H}_2\text{P}_2\text{O}_2$, $\text{NaH}_2\text{P}_2\text{O}_2 \cdot \text{H}_2\text{O}$, $(\text{NH}_4)_2\text{H}_2\text{P}_2\text{O}_2$, $\text{KH}_2\text{P}_2\text{O}_2$, $\text{Ca}(\text{H}_2\text{P}_2\text{O}_2)_2$, $\text{Mg}(\text{H}_2\text{P}_2\text{O}_2)_2$, $\text{Co}(\text{H}_2\text{P}_2\text{O}_2)_2 \cdot 6\text{H}_2\text{O}$, $\text{Mn}(\text{H}_2\text{P}_2\text{O}_2)_2 \cdot \text{H}_2\text{O}$, $\text{Zn}(\text{H}_2\text{P}_2\text{O}_2)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Pb}(\text{H}_2\text{P}_2\text{O}_2)_2$. Of these $\text{NaH}_2\text{P}_2\text{O}_2 \cdot \text{H}_2\text{O}$ is the most preferred because of the high solubility, nontoxicity and ease of availability.

As can be seen, the precise natures of the anion of the Zr-containing salt and the cation of the hypophosphite are not critical and need only be compatible with the underlying process.

Examples of the water-soluble manganese compounds are $\text{CoCl}_2 \cdot 4\text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{Co}(\text{CH}_3\text{COO})_2$.

Examples of the water-soluble manganese compounds are $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, $\text{Mn}(\text{NO}_3)_2 \cdot n\text{H}_2\text{O}$, $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$ and $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$.

$\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$, $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Ce}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ and $\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ are examples of the water-soluble cerium compounds.

In a preferred embodiment of the processes for producing pearlescent pigment of this invention, an aqueous solution of a hypophosphite is slowly added to an aqueous solution of a zirconium or zirconyl compound at a temperature lower than 50° C. with stirring so as not to form white precipitate, and hydrochloric acid is added to the clear solution thus obtained, affording a mixed solution of the hypophosphite and the zirconium or zirconyl salt. Separately, a base material is slurried in water to a concentration of 5 to 15 weight %, the slurry is then heated with stirring to a temperature from 50° C. to its boiling point, and its pH is adjusted to 2 to 6 by addition of hydrochloric acid or the like. To this slurry, is added an aqueous solution of a water-soluble compound (or compounds) of at least one member selected from cobalt, manganese and cerium as mentioned above. The solution of hypophosphite and zirconium (or zirconyl) compound prepared above is then added dropwise with stirring at a constant rate while maintaining the pH at a constant level within the range from 2 to 6 by addition of an aqueous alkaline solution (e.g., a caustic soda solution), and the mixture is stirred at that temperature for at least 30 minutes. After raising the pH to a level of 5 to 9 by addition of an aqueous alkaline solution (e.g., a caustic soda solution), stirring is further continued at that temperature for at least 30 minutes, and the reaction product is collected by filtration, washed with water and dried at 80° to 130° C.

In a second embodiment of the manufacturing processes of this invention, an aqueous solution of hypophosphite is slowly added to an aqueous solution of a zirconium or zirconyl compound at a temperature lower than 50° C. with stirring so as not to form white precipitate, and hydrochloric acid is added to this clear solution to afford a mixed solution of the hypophosphite and the zirconium or zirconyl salt. Separately, a base material is slurried in water to a concentration of 5 to 15 weight %, the slurry is then heated with stirring to a temperature from 50° C. to its boiling point, and its pH is adjusted to 2 to 6 by addition of hydrochloric acid or the like. To this slurry is added dropwise with stirring the solution of a hypophosphite and a zirconium (or zirconyl) compound prepared above at a constant rate while maintaining the pH at a constant level within the range from 2 to 6 by addition of an aqueous alkaline solution (e.g., a caustic soda solution), and the mixture is stirred at that temperature for at least 30 minutes. An aqueous solution of a water-soluble compound (or compounds) of at least one member selected from cobalt, manganese and cerium as mentioned above is then added, the pH is raised to a level of 4 to 9 by addition of an aqueous alkaline solution (e.g., caustic soda solution), stirring is further continued at that temperature for at least 30 minutes and the reaction product is collected by filtration, washed with water and dried at 80° to 130° C.

In a third embodiment of the manufacturing processes of this invention, base material is slurried in water to a concentration of 5 to 15 weight %, the slurry is then heated with stirring to a temperature from 50° C. to its boiling point, and its pH is adjusted to 2 to 6 by addition of hydrochloric acid or the like. To this slurry is added an aqueous solution of a water-soluble compound (or compounds) of at least one member selected from cobalt, manganese and cerium as mentioned above the pH is then raised to a level of 4 to 9 by addition of an aque-

ous alkaline solution (e.g., a caustic soda solution), and stirring is continued at that temperature for at least 30 minutes. Separately, an aqueous solution of a hypophosphite is slowly added to an aqueous solution of a zirconium or zirconyl compound at a temperature lower than 50° C. with stirring so as not to form white precipitate, and hydrochloric acid is added to this clear solution to afford a mixed solution of the hypophosphite and the zirconium or zirconyl salt. This solution is added dropwise with stirring to the slurry prepared above at a constant rate while maintaining the pH at a constant level within the range from 2 to 6 by addition of an aqueous alkaline solution (e.g., a caustic soda solution), and the mixture is stirred at that temperature for at least 30 minutes. After raising the pH to a level of 5 to 9 by addition of an aqueous alkaline solution (e.g., an aqueous solution of caustic soda), stirring is continued at that temperature for at least 30 minutes, and the reaction product is collected by filtration, washed with water and dried at 80° to 130° C.

In the processes for producing weather-resistant pearlescent pigment of this invention, methods other than that described above may also be adopted for the formation of hydrated zirconium oxide. For example, an aqueous slurry of base material is adjusted to pH 1 to 2 with hydrochloric acid or the like, an aqueous solution of a zirconium or zirconyl salt is added with stirring, and then an aqueous solution of a hypophosphite is slowly added while maintaining the temperature in the range from 50° C. to the boiling point of said slurry. Stirring is continued at that temperature for some time, and an aqueous alkaline solution (e.g., a caustic soda solution) is slowly added by means of a metering feeder to raise the pH of slurry to a level of 4 to 9.

In another method, an aqueous solution of a zirconium or zirconyl salt and an aqueous solution of a hypophosphite are separately added dropwise with stirring each at a constant rate and at a definite proportion to an aqueous slurry of base material while holding the temperature within the range from 50° C. to the boiling point of said slurry and maintaining the pH at a constant level within the range of 2 to 6 by addition of an aqueous alkaline solution (e.g., a caustic soda solution). Stirring is continued at that temperature for at least 30 minutes, and the pH is raised to a level of 5 to 9 by addition of an aqueous alkaline solution (e.g., a caustic soda solution).

In the manufacturing processes of this invention, the water-soluble salt capable of forming hydrated zirconium oxide is used generally in an amount of 0.001 to 0.05 mole, preferably 0.005 to 0.03 mole, per 100 g of the base pigment, and the hypophosphite is used in such an amount that the atomic ratio of phosphorus to zirconium will be in the range from 1:2 to 10:1, preferably from 1:1 to 3:1.

The amount of water-soluble compound of cobalt, manganese or cerium, when used alone, is 0.003 to 0.03 mole, preferably 0.007 to 0.015 mole, for cobalt compound; 0.001 to 0.01 mole, preferably 0.003 to 0.007 mole, for manganese compound; and 0.0006 to 0.006 mole, preferably 0.001 to 0.004 mole, for cerium compound (each per 100 g of base pigment).

The amount of hydrated zirconium oxide deposited on the pigment substrate is typically about 0.1-6% by weight based on the pigment and calculated as ZrO_2 , preferably about 0.5-4% by weight.

The hydrated oxide of cobalt assumes a blue to green color, that of manganese a brown color, and that of

cerium white to faint yellow color. Hence, various desired colors be obtained by using these oxides either alone or in combination.

In the above-mentioned manufacturing processes, the solution of zirconium or zirconyl salt may also contain other types of metal salts, such as a water-soluble salt of aluminum, zinc, tin, cobalt, manganese and cerium. In addition, an aluminate, zincate, silicate or phosphate may also be added to the aqueous solution of hypophosphite and/or to the aqueous alkaline solution in an amount that allows the formation of hydrated zirconium oxide.

Furthermore, the base pigment on which hydrated zirconium oxide has been deposited may be treated with a coupling agent (e.g., a silane coupling agent) to further improve the water resistance of the pearlescent pigment of this invention and to ensure its higher affinity for coating materials.

Silane coupling agents are known as compounds which act upon the interface between an organic material and an inorganic material, thereby enhancing the affinity between the two.

Illustrative examples of silane coupling agents include γ -(2-aminoethyl)aminopropyl-trimethoxysilane, γ -(2-aminoethyl)aminopropyl-methyl-dimethoxysilane, γ -methacryloxypropyl-methyl-trimethoxysilane, γ -glycidoxypolytrimethoxysilane, γ -mercaptopropyl-trimethoxysilane, vinyltriacetoxysilane, γ -chloropropyltrimethoxysilane, vinyltrimethoxysilane, octadecyldimethyl-[3-(trimethoxysilyl)-propyl]ammonium chloride, γ -mercaptopropyl-methyl-dimethoxysilane, methyl-trichlorosilane, dimethyl-dichlorosilane and trimethyl-chlorosilane. In actual practice, a compound having a functional group suited for the organic vehicle to be combined with the pigment, under consideration is selected. For example, γ -(2-aminoethyl)aminopropyltrimethoxysilane, γ -methacryloxypropyl-trimethoxysilane and γ -glycidoxypoly-trimethoxysilane are suitable for acrylic vehicles.

The treatment is effected by adding a solution of a silane coupling agent in water, or in a mixture of water and an organic solvent, to an aqueous slurry of pearlescent pigment coated with hydrated zirconium oxide, stirring the mixture for at least 15 minutes, and collected the treated powder by filtration, followed by washing with water and drying at 80° to 130° C.

The treating solution used above should contain 0.1 to 3%, preferably 0.5 to 2%, of the silane coupling agent based on the weight of pigment being treated, and the concentration of the agent should be in the range from 0.1 to 5 weight %.

The pearlescent pigment of this invention thus prepared shows weatherability sufficiently high to be employed as a colorant of paint for outdoor use, particularly exterior paint for case, and its dispersibility remains high, with no adverse effect at all upon the color tone and gloss of the base pigment.

The pearlescent pigment of this invention can be applied not only to paint for outdoor use, but also to many other materials used outdoors, such as plastics, and as a colorant for printing inks.

Without further elaboration, it is believed that one skilled in the art can, using the preceding description, utilize the present invention to its fullest extent. The following preferred specific embodiments are, therefore, to be construed as merely illustrative, and not limitative of the remainder of the disclosure in any way whatsoever.

In the foregoing and in the following examples, all temperatures are set forth uncorrected in degrees Celsius and unless otherwise indicated, all parts and percentages are by weight.

The entire texts of all applications, patents and publications, if any, cited above and below, and of corresponding application Japanese No. 63-120689 filed May 19, 1988, are hereby incorporated by reference.

The properties of pigments obtained in these Examples are listed in Table 1 shown later.

EXAMPLES

Example 1

A 1 wt-% aqueous solution containing 1.88 g sodium hypophosphite ($\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$) was added at room temperature with stirring to a 10 wt-% aqueous solution containing 2.88 g of zirconium oxychloride ($\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$) so slowly as not to form any white precipitate. To the clear solution thus obtained, as added 30 g of 3.5 wt-% hydrochloric acid, affording a mixed solution of zirconium oxychloride and sodium hypophosphite.

Separately, 50 g of mica flakes coated with rutile titanium dioxide (about 48% based on the total weight) having a particle size of 10 to 50 μ and showing blue reflection color and yellow transmission color (Triodin 225 Rutile Blue; product of E. Merck) were suspended in 500 ml water, and the slurry thus obtained was heated to 75° C. with stirring. The pH was adjusted to 3 by addition of hydrochloric acid, 1 wt-% aqueous solution containing 0.567 g cerium chloride ($\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$) was added, and then the mixed solution of zirconium oxychloride and sodium hypophosphite prepared above was added dropwise at a rate of 4 ml/min while maintaining the pH at 3 by addition of 1 wt-% aqueous solution of caustic soda. Stirring was continued at 75° C. for 30 minutes.

The solid matters were collected by filtration, washed with water and dried at 120° C.

The solid product thus obtained was grayish-white, pearlescent pigment with good dispersibility showing blue reflection color and yellow transmission color.

Example 2

Fifty grams of mica flakes coated with rutile titanium dioxide (the same type as used in Example 1) were treated in much the same manner as in Example 1) were treated in much the same manner as in Example 1, except that 0.756 g cobalt sulfate ($\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$) was used in place of 0.567 g cerium chloride ($\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$).

The solid product thus obtained was greenish-white, pearlescent pigment with good dispersibility showing blue reflection color and yellow transmission color.

Example 3

Fifty grams of mica flakes coated with rutile titanium dioxide (the same type as used in Example 1) were treated in much the same manner as in Example 1, except that 0.625 g manganese sulfate ($\text{MnSO}_4 \cdot 4.5\text{H}_2\text{O}$) was used in place of 0.567 g cerium chloride ($\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$).

The solid product thus obtained was orangy-white, pearlescent pigment with good dispersibility showing blue reflection color and yellow transmission color.

Example 4

Fifty grams of mica flakes coated with rutile titanium dioxide (the same type as used in Example 1) were treated in much the same manner as in Example 1, ex-

cept that 0.0625 g manganese sulfate ($\text{MnSO}_4 \cdot 4.5\text{H}_2\text{O}$) and 0.454 g cobalt sulfate ($\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$) were used in place of 0.567 g cerium chloride ($\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$).

The solid product thus obtained was faint orangy-white, pearlescent pigment with good dispersibility showing blue reflection color and yellow transmission color.

Example 5

A 1 wt-% aqueous solution containing 1.88 g sodium hypophosphite ($\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$) was added at room temperature with stirring to a 10 wt-% aqueous solution containing 2.88 g zirconium oxychloride ($\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$) so slowly as not to form any white precipitate. To the clear solution thus obtained, was added 30 g of 3.5 wt-% hydrochloric acid, affording a mixed solution of zirconium oxychloride and sodium hypophosphite.

Separately, 50 g of mica flakes coated with rutile titanium dioxide (the same type as used in Example 1) were suspended in 500 ml water, and the slurry thus obtained was heated to 75° C. with stirring. After adjusting the pH to 3 by addition of hydrochloric acid, the mixed solution of zirconium oxychloride and sodium hypophosphite prepared above was added dropwise at a rate of 4 ml/min while maintaining the pH at 3 by addition of 1 wt-% aqueous solution of caustic soda. Stirring was continued at 75° C. for 30 minutes, 1 wt-% aqueous solution containing 0.567 g cerium chloride ($\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$) was added, then 1 wt-% aqueous solution of caustic soda was added dropwise at a rate of 2.4 ml/min until the pH reached 7.2, and stirring was further continued at 75° C. for 30 minutes.

The solid matters were collected by filtration, washed with water and dried at 120° C.

The solid product thus obtained was grayish-white, pearlescent pigment with good dispersibility showing blue reflection color and yellow transmission color.

Example 6

Fifty grams of mica flakes coated with rutile titanium dioxide (the same type as used in Example 1) were suspended in 500 ml water, and the slurry thus obtained was heated to 75° C. with stirring. After adjusting the pH to 3 by addition of hydrochloric acid, 1 wt-% aqueous solution containing 0.567 g cerium chloride ($\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$) was added, then 1 wt-% aqueous solution of caustic soda was added dropwise at a rate of 2.4 ml/min until the pH reached 7.2, and stirring was further continued at 75° C. for 30 minutes.

Separately, 1 wt-% aqueous solution containing 1.88 g sodium hypophosphite ($\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$) was added at room temperature with stirring to a 10 wt-% aqueous solution containing 2.88 g of zirconium oxychloride ($\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$) so slowly as not to form any white precipitate. To the clear solution thus obtained, was added 30 g of 3.5 wt-% hydrochloric acid, affording a mixed solution of zirconium oxychloride and sodium hypophosphite. This solution was added dropwise to the slurry prepared above at a rate of 4 ml/min while maintaining the pH at 3 by addition of 1 wt-% aqueous solution of caustic soda, stirring was continued at 75 for 30 minutes, 1 wt-% aqueous solution of caustic soda was added dropwise at a rate of 2.4 ml/min until the pH reached 7.2, and stirring was further continued at 75° C. for 3 minutes.

The solid matters were collected by filtration washed with water and dried at 120° C.

The solid product thus obtained was grayish-white, pearlescent pigment with good dispersibility showing blue reflection color and yellow transmission color.

Example 7

Fifty grams of mica flakes coated with rutile titanium dioxide (the same type as used in Example 1) were suspended in 500 ml water, and the slurry thus obtained was heated to 75° C. with stirring. After adjusting the pH to 1.6 by addition of hydrochloric acid, 1 wt-% aqueous solution containing 0.567 g cerium chloride ($\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$) and 10 wt-% aqueous solution containing 2.88 g zirconium oxychloride ($\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$) were added. A 1 wt-% aqueous solution containing 1.88 g sodium hypophosphite ($\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$) was then added with stirring at a rate of 3.1 ml/min, stirring was continued at 75° C. for 30 minutes, 1 wt-% aqueous solution of caustic soda was added dropwise at a rate of 5.3 ml/min until the pH reached 7.2, and stirring was further continued at 75° C. for 30 minutes.

The solid matters were collected by filtration, washed with water and dried at 120° C.

The solid product thus obtained was grayish-white, pearlescent pigment with good dispersibility showing blue reflection color and yellow transmission color.

Example 8

Fifty grams of mica flakes coated with rutile titanium dioxide (the same type as used in Example 1) were treated in much the same manner as in Example 1. To the slurry of solid product before filtration, was added 1 wt-% aqueous solution containing 0.5 g of γ -glycidoxypentyltrimethoxy-silane (a silane coupling agent, SH6040; product of Toray Silicone Inc.), and the mixture was stirred at 75° C. for 30 minutes.

The solid matters were collected by filtration and dried at 120° C.

The solid product thus obtained was grayish-white, pearlescent pigment with good dispersibility showing blue reflection color and yellow transmission color.

Streamlines were observed when this pigment was suspended in an organic solvent of low polarity (e.g., toluene), indicating its enhanced affinity for organic substances.

Example 9

Fifty grams of mica flakes coated with rutile titanium dioxide (about 28% based on the total weight) having a particle size of 10 to 50 μ and showing grayish-white base color and white reflection color (Triodin 103 Sterling Silver; product of E. Merck) were treated in the same manner as in Example 8.

The solid product thus obtained was grayish-white, pearlescent pigment with good dispersibility showing white reflection color.

Streamlines were observed when this pigment was suspended in an organic solvent of low polarity (e.g., toluene), indicating its enhanced affinity for organic substances.

Example 10

Fifty grams of mica flakes coated with titanium dioxide and iron oxide (approximately 36% and 8%, respectively, based on the total weight) having a particle size of 10 to 50 μ and showing yellow base color and gold reflection color (Triodin 300 Gold pearl; product of E. Merck) were suspended in 500 ml water, and the slurry thus obtained was heated to 75° C. with stirring. After

adjusting the pH to 3 by addition of hydrochloric acid, 1 wt-% aqueous solution containing 0.567 g cerium chloride ($\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$) and 1 wt-% aqueous solution containing 0.41 g zinc chloride (ZnCl_2) were added.

5 Separately, a 1 wt-% aqueous solution containing 1.88 g sodium hypophosphite ($\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$) was added at room temperature with stirring to a 10 wt-% aqueous solution containing 2.88 g zirconium oxychloride ($\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$) so slowly as not to form any white precipitate. To the clear solution thus obtained, was added 30 g of 3.5 wt-% hydrochloric acid, affording a mixed solution of zirconium oxychloride and sodium hypophosphite. This solution was added dropwise to the slurry prepared above at a rate of 4 ml/min while maintaining the pH at 3 by addition of 1 wt-% aqueous solution of caustic soda, stirring was continued at 75° C. for 30 minutes, 1 wt-% aqueous solution of caustic soda was added dropwise at a rate of 2.4 ml/min until the pH reached 7.2, and stirring was further continued at 75° C. for 30 minutes. To the slurry thus obtained, was added 1 wt-% aqueous solution of γ -(2-aminoethyl)amino-propyltrimethoxy silane (a silane coupling agent, SH6020; product of Toray Silicone Inc.), and stirring was continued at 75° C. for 30 minutes.

25 The solid matters were collected by filtration, washed with water and dried at 120° C.

The solid product thus obtained was yellow, pearlescent pigment with good dispersibility showing gold reflection color.

30 Streamlines were observed when this pigment was suspended in an organic solvent of low polarity (e.g., toluene), indicating its enhanced affinity for organic substances.

Comparative Example 1 (dispersibility when hypophosphite is not used)

Fifty grams of mica flakes coated with rutile titanium dioxide (the same type as used in Example 1) was suspended in 500 ml water, the slurry thus obtained was heated to 75° with stirring, the pH was adjusted to 1.6 by addition of hydrochloric acid, and 10 wt-% aqueous solution containing 2.88 g zirconium oxychloride ($\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$) was added. To the resulting slurry, was added dropwise 1 wt-% aqueous caustic soda solution with stirring at a rate of 5.3 ml/min until the pH reached 7.2, and stirring was continued at 75° C. for 30 minutes.

The solid product was collected by filtration, washed with water and dried at 120° C., giving grayish-white powder containing small lumps.

Comparative Example 2 (dispersibility when no cerium compound is used)

Fifty grams of mica flakes coated with rutile titanium dioxide (the same type used in Example 1) was suspended in 500 ml water, the slurry thus obtained was heated to 75° C. with stirring, the pH was adjusted to 1.6 by addition of hydrochloric acid, and 10 wt-% aqueous solution containing 2.88 g zirconium oxychloride ($\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$) was added. To the resulting slurry, was added dropwise with stirring a 1 wt-% aqueous solution containing 1.88 g sodium hypophosphite ($\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$) at a rate of 3.1 ml/min, and the mixture was stirred at 75° C. for 30 minutes. A 1 wt-% aqueous caustic soda solution was then added with stirring at a rate of 5.3 ml/min until the pH reached 7.2, and stirring was further continued at 75° C. for 30 minutes. A 1 wt-% aqueous solution containing 0.5 g γ -glycidoxypentyltrimethoxy-silane (a silane coupling agent, SH6040; product of Toray Silicone Inc.) was added dropwise with stirring at a rate of 3.1 ml/min, and the mixture was stirred at 75° C. for 30 minutes.

propyltrimethoxysilane was then added, and the mixture was stirred at 75° C. for 30 minutes.

The solid matters were collected by filtration, washed with water and dried at 120° C.

The solid product thus obtained was grayish-white, pearlescent pigment with good dispersibility showing blue reflection color and yellow transmission color.

Test Examples

The pigments prepared in the above Examples and Comparative Examples were evaluated according to the methods described below. The results obtained are summarized in Table.

Testing of Water Resistance (Hot-water Immersion Test)

One part by weight of a pigment sample was mixed with nine parts of a thermosetting acrylic/melamine resin (a 7:3 mixture of Acrylic 47-712 and Superbeckamine G821-60; product of Dainippon Ink & Chemicals, Inc.). Separately, a black enamel (Superlac F-47; product of Nippon Paint Co., Ltd.) was coated on a steel plate previously treated with zinc phosphate (7 cm × 15 cm) to a thickness of about 25 μm (on dry basis) and baked at 150° C. for 20 minutes. On this enamel-coated plate, was coated the pigmented thermosetting resin prepared above to a thickness of about 20 μm (on dry basis), followed by wet-on-wet application of a clear topcoating (a 7:3 mixture of Acrylic 44-179 and Superbeckamine L17-60; product of Dainippon Ink & Chemicals, Inc.) to a thickness of about 30 μm (on dry basis) and baking at 140° C. for 18 minutes.

The test plate thus prepared was immersed in 80° C. hot water for three hours, the hot water was allowed to cool slowly to room temperature, the treated plate was taken out, and the changes in appearance were evaluated by visual observation. The figures in the table represent the degrees of chalking (water resistance); "5" indicates no chalking (the highest water resistance), and decreasing figures show increasing degrees of chalking (lowering water resistance).

Testing of Light Resistance

Three parts by weight of a pigment sample was mixed with 100 parts of a polyvinyl chloride resin compound having the following composition, the mixture was kneaded on a twin roll at 175° C. for 10 minutes, and the kneaded product was pressed at 175° C. for two minutes under a pressure of 45 Kg/cm² into 1.0 mm thick specimens.

(polyvinyl chloride resin compound)	parts by wt.
PVC resin with number average M.W. of 1650 (Zeon 121; Nippon Zeon Co., Ltd.)	1000
PVC resin with number average M.Z. of 1100 (Zeon 131; Nippon Zeon Co., Ltd.)	1000
Acrylic Processing aid for PVC resin (Methablene P-351; Mitsubishi Rayon Co., Ltd.)	40
Tribasic lead sulfate, 3PbO.PbSO ₄ .H ₂ O	60
Dibasic lead stearate, 2PbO.Pb(C ₁₇ H ₃₅ COO) ₂	20
Mono-olein, C ₁₇ H ₃₃ COOCH ₂ CH(OH)CH ₂ OH	20

A specimen prepared above was subjected to an accelerated exposure test for three hours (12 minutes of precipitation in every 60 minutes of irradiation; black panel temperature: 63° ± 3° C.) using a carbon-arc, sunshine weatherometer (Model WEL-SUN-HC of Suga Tester Co., Ltd.). The treated specimen was then allowed to stand for 24 hours in a cold and dark place,

and the difference in blackening degree from an untreated specimen was evaluated by using a gray scale.

This test is to evaluate the degree of activity exhibited by titanium dioxide in the presence of water under irradiation of near ultraviolet rays. It utilizes the fact that the lead ions contained in a specimen are reduced to metallic lead by the action of titanium dioxide in the presence of mon-olein, thus blackening the specimen.

Weatherability (Accelerated Exposure) Test

A test plate prepared above for the water-resistance test was subjected to an accelerated exposure test for 120 hours (12 minutes of precipitation in every 60 minutes of irradiation; black panel temperature: 63° ± 3° C.) in the same carbon-arc, sunshine weatherometer was used above. The color of the treated plate was measured by using a differential colorimeter (Model D-25 of Hunter Laboratories, and the color difference before and after the test (ΔE) was calculated.

TABLE I

Sample	Water Resistance	Light Resistance	Weatherability (E)
<u>Example</u>			
1	4	4-5	—
2	4	4-5	—
3	4	5	—
4	4	4-5	—
5	4	4-5	—
6	4	4-5	—
7	4	4-5	—
8	5	4-5	1.1
9	5	4-5	0.2
10	5	5	0.2
<u>Comp. Ex.</u>			
1	3	—	—
2	4	1-2	1.7
<u>Iriodin</u>			
225	1	1	3.7
103	1	1-2	0.7
300	1	5	—

The preceding examples can be repeated with similar success by substituting the generically or specifically described reactants and/or operating conditions of this invention for those used in the preceding examples.

From the foregoing description, one skilled in the art can easily ascertain the essential characteristics of this invention, and without departing from the spirit and scope thereof, can make various changes and modifications of the invention to adapt it to various usages and conditions.

What is claimed is:

1. A process for the production of a weather-resistant nacreous pigment, comprising hydrolyzing a zirconium or zirconyl compound, in the presence of a hypophosphite and a metal oxide-coated mica flake pigment, whereby a hydrated zirconium oxide is deposited onto the surface of the metal oxide-coated mica flake, and coating onto said mica flake with said hydrated zirconium oxide a hydrated metal oxide of cobalt, manganese or cerium.

2. A process according to claim 1, comprising simultaneously depositing, in an aqueous medium, on the surface of metal oxide coated mica flakes, a mixture of hydrated metal oxides formed by hydrolysis of a zirconyl compound and at least one water-soluble compound of cobalt, manganese or cerium, in the presence of a hypophosphite.

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3. A process according to claim 1, comprising depositing in an aqueous medium, on the surface of metal oxide coated mica flakes, a hydrated metal oxide formed by hydrolysis of a water-soluble compound of at least one of cobalt, manganese and cerium; and subsequently depositing a hydrated zirconium oxide by hydrolysis of a zirconium compound in the presence of a hypophosphite.

4. A process according to claim 1, wherein the pigment is a mica flake coated with an oxide of Ti, Fe, Sn, Cr, Zr or a mixture thereof.

5. A process according to claim 4, wherein the pigment is a mica flake coated with rutile TiO_2 or with an iron oxide containing a titanium oxide.

6. A process according to claim 1, wherein a salt of hypophosphorous acid and a salt capable of forming zirconium oxide under hydrolysis conditions are dissolved in an aqueous slurry of a metal oxide-coated mica flake pigment, and the salt capable of forming zirconium oxide is hydrolyzed so as to deposit hydrated zirconium oxide onto the surface of the metal oxide-coated mica flake.

7. A process according to claim 6, wherein the salt capable of forming zirconium oxide is ZrCl_4 , $\text{Zr}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$, $\text{Zr}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$, $\text{ZrOCl}_2 \cdot \text{H}_2\text{O}$, $\text{ZrO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$, $\text{ZrOSO}_4 \cdot 4\text{H}_2\text{O}$ or $\text{ZrO}(\text{CH}_3\text{COO})_2$.

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8. A process according to claim 6, wherein the salt of hypophosphorous acid is HPH_2O_2 , $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$, $(\text{NH}_4)\text{H}_2\text{PO}_2$, KH_2PO_2 , $\text{Ca}(\text{H}_2\text{PO}_2)_2$, $\text{Mg}(\text{H}_2\text{PO}_2)_2$, $\text{Co}(\text{H}_2\text{PO}_2)_2 \cdot 6\text{H}_2\text{O}$, $\text{MN}(\text{H}_2\text{PO}_2)_2 \cdot \text{H}_2\text{O}$, $\text{Zn}(\text{H}_2\text{PO}_2)_2 \cdot 6\text{H}_2\text{O}$ or $\text{Pb}(\text{H}_2\text{PO}_2)_2$.

9. A process according to claim 6, wherein the salt capable of forming zirconium oxide is $\text{ZrOCl}_2 \cdot \text{H}_2\text{O}$ and the salt of hypophosphorous acid is $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$.

10. A method of improving the water resistance, light-fastness and dispersibility of a nacreous pigment containing metal oxide-coated mica particles, comprising coating said particles with hydrated zirconium oxide and a hydrated oxide of at least one of cobalt, manganese or cerium, in the presence of a hypophosphite.

11. A process according to claim 1, wherein a silane coupling agent in aqueous solution is added under stirring to a resultant aqueous slurry containing the metal oxide-containing mica flake pigment once hydrated zirconium oxide is deposited on the surface thereof.

12. In a process for the preparation of a paint or glaze composition, comprising combining a nacreous pigment and paint or glaze components, the improvement wherein the nacreous pigment is prepared according to claim 1.

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(51) Internationale Patentklassifikation ⁶ : C09C 1/00, C09D 7/12, C08K 3/00, A61K 7/00, C04B 33/14, C03C 4/02, C09D 11/00	A1	(11) Internationale Veröffentlichungsnummer: WO 99/20695 (43) Internationales Veröffentlichungsdatum: 29. April 1999 (29.04.99)
(21) Internationales Aktenzeichen: PCT/EP98/06508 (22) Internationales Anmeldedatum: 14. Oktober 1998 (14.10.98) (30) Prioritätsdaten: 197 46 067.4 17. Oktober 1997 (17.10.97) DE (71) Anmelder (für alle Bestimmungsstaaten ausser US): MERCK PATENT GMBH [DE/DE]; Frankfurter Strasse 250, D-64293 Darmstadt (DE). (72) Erfinder; und (75) Erfinder/Anmelder (nur für US): SCHMIDT, Christoph [DE/DE]; Taunusstrasse 33 A, D-65830 Kriefel (DE). PFAFF, Gerhard [DE/DE]; Trautenauer Strasse 41, D-64839 Münster (DE). SCHANK, Christina [DE/DE]; Bahnhofstrasse 39, D-64367 Mühltal (DE). SCHOEN, Sabine [DE/DE]; Gundolfstrasse 25, D-64287 Darmstadt (DE). (74) Gemeinsamer Vertreter: MERCK PATENT GMBH; Post- fach, D-64271 Darmstadt (DE).	(81) Bestimmungsstaaten: CN, JP, KR, MX, US, europäisches Patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Veröffentlicht <i>Mit internationalem Recherchenbericht. Vor Ablauf der für Änderungen der Ansprüche zugelassenen Frist; Veröffentlichung wird wiederholt falls Änderungen eintreffen.</i>	
(54) Title: INTERFERENCE PIGMENTS (54) Bezeichnung: INTERFERENZPIGMENTE (57) Abstract <p>The invention relates to interference pigments with a base consisting of multicoated platelet-shaped substrates with a sequence of layers made up of A) a coating with at least one refraction index $n \geq 2.0$, B) a colourless coating with a refraction index $n \leq 1.8$, and C) a non-absorbent high-refraction coating, and optionally, D) an outer protection layer.</p> (57) Zusammenfassung <p>Die vorliegende Erfindung betrifft Interferenzpigmente auf der Basis von mehrfach beschichteten plättchenförmigen Substraten, die mindestens eine Schichtenfolge aus: (A) einer Beschichtung mit einem Brechungsindex $n \geq 2.0$, (B) einer farblosen Beschichtung mit einem Brechungsindex $n \leq 1.8$, und (C) einer nicht absorbierenden hochbrechenden Beschichtung, sowie gegebenenfalls, (D) eine äußere Schutzschicht aufweisen.</p>		

LEDIGLICH ZUR INFORMATION

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Interferenzpigmente

Die vorliegende Erfindung betrifft Interferenzpigmente auf der Basis von mehrfach beschichteten plättchenförmigen Substraten.

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Glanz- oder Effektpigmente werden in vielen Bereichen der Technik eingesetzt, insbesondere im Bereich der Autolacke, der dekorativen Beschichtung, im Kunststoff, in Farben, Druckfarben sowie in kosmetischen Formulierungen.

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Glanzpigmente, die einen winkelabhängigen Farbwechsel zwischen mehreren Interferenzfarben zeigen, sind aufgrund ihres Farbenspiels von besonderem Interesse für Autolacke sowie bei fälschungssicheren Wertschriften. Derartige Pigmente sind auf Basis von mehrfach beschichteten plättchenförmigen Substraten bekannt.

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Interferenzpigmente bestehen in der Regel aus 200 bis 1000 nm dicken plättchenförmigen Substraten, die mit 50 bis 300 nm dicken, stark lichtbrechenden Metalloxiden bzw. Metalloxidgemischen überzogen sind. Die optischen Eigenschaften dieser Pigmente werden in entscheidendem Maße durch den Brechungsindex der Metalloxidschicht bestimmt. Neben der Möglichkeit über Chemical Vapor Deposition (CVD)- oder Physical Vapor Deposition (PVD)-Verfahren Metalloxidschichten herzustellen, die hohe Dichten und damit nahe am Optimum liegende Brechungsindizes aufweisen, erfolgt die Abscheidung von Metalloxiden auf feinteiligen, plättchenförmigen Substraten häufig durch Titration von wäßrigen, meist sauren Metallsalzlösungen gegen Natronlauge in Gegenwart eines Substrates, wie z.B. in den DE 14 67 468 und DE 20 09 566 beschrieben.

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Nachteil des Aufdampfverfahrens sind die damit verbundenen hohen Kosten. So ist aus der U.S. 4,434,010 ein mehrschichtiges Interferenzpigment bekannt bestehend aus einer zentralen Schicht eines reflektierenden Metalls, wie z.B. Aluminium, und alternierenden Schichten zweier transparenter dielektrischer Materialien mit hohem und niedrigem Brechungsindex, wie z.B., Titandioxid und Siliziumdioxid. Dieses Mehrschichtpigment wird vorzugsweise für fälschungssichere Wertpapiere verwendet.

- Aus der JP H7-759 ist ein mehrschichtiges Interferenzpigment mit metallischem Glanz bekannt, wobei ein Substrat mit alternierenden Schichten von Titandioxid und Siliziumdioxid beschichtet ist. Als Substrat werden Aluminium-, Gold- oder Silberflakes, oder Plättchen aus Glimmer bzw. Glas, die mit Metallen beschichtet sind, eingesetzt. Der für Interferenzpigmente charakteristische und erwünschte Tiefeneffekt kann allerdings nicht erzeugt werden. Dafür ist die Totalreflexion des Lichtes an der den Kern bildenden Metallschicht verantwortlich. Der Interferenzeffekt bleibt deshalb auf die sich auf der Metallschicht befindlichen Schichten begrenzt. Darüber hinaus werden aufgrund der fehlenden Transparenz des Substrates die vielfältigen Kombinationsmöglichkeiten mit weiteren Pigmenten in anwendungstechnischen Formulierungen stark eingeschränkt.
- In den US 3,438,796 und US 5,135,812 werden zum Beispiel metallische Glanzpigmente beschrieben, die einen zentralen opaken Aluminiumfilm aufweisen, der beidseitig alternierend mit dielektrischen niedrigbrechenden Filmen, wie z.B. Siliziumdioxid oder Magnesiumfluorid, und teilweise transparenten Metallfilmen, wie z.B. Chrom oder Aluminium, beschichtet ist. Aufgrund des Herstellungsverfahrens ist der zentrale Metallfilm dieser Pigmente nur an der Plättchenober- und -unterseite beschichtet, während die Seitenflächen Bruchkanten darstellen und zum Medium hin offen liegen.
- Aus der DE 44 05 494, DE 44 37 753, DE 195 16 181 und DE 195 15 988 sind Glanzpigmente bekannt, die durch Beschichtung von Metallplättchen, insbesondere Aluminiumflakes, über CVD-Verfahren oder naßchemisch mit niedrigbrechenden Metalloxidschichten, wie z.B. einer Siliziumdioxidschicht, und nicht selektiv absorbierenden hochbrechenden Metalloxidschichten bzw. Metallschichten hergestellt werden.
- Glanzpigmente auf Basis von Metallsubstraten weisen häufig gute Anwendungseigenschaften, u.a. ein gutes Deckvermögen auf, jedoch resultiert bei der Applikation, z.B. im Lack, ein "harter" metallischer Glanz, der häufig nicht erwünscht ist.

- 5 Glanzpigmente auf Basis transparenter plättchenförmiger Substrate, die diesen "harten" metallischen Glanz nicht aufweisen, sind Gegenstand der WO 93/12182. Glimmerplättchen werden mit einer hochbrechenden Metalloxidschicht, wie z.B. TiO_2 , und einer nicht selektiv absorbierenden Schicht belegt. Diese Pigmente zeigen in Abhängigkeit von der TiO_2 -Schichtdicke in der Aufsicht eine bestimmte Interferenzfarbe, die mit schräger werdendem Blickwinkel zunehmend schwächer wird und schließlich nach grau bzw. schwarz abkippt. Die Interferenzfarbe ändert sich nicht, aber es ist eine Abnahme der Farbsättigung festzustellen.
- 10 In der JP 1992/93206 werden Glanzpigmente auf Basis von Glasflakes bzw. Glimmerpartikeln beansprucht, die mit einer opaken Metallschicht und alternierenden SiO_2 - und TiO_2 -Schichten belegt sind.
- 15 Aus der EP 0 753 545 sind Glanzpigmente auf Basis von mehrfach beschichteten, hochbrechenden, für sichtbares Licht zumindest teilweise durchlässigen, nichtmetallischen, plättchenförmigen Substraten bekannt, die mindestens ein Schichtpaket aus einer farblosen niedrigbrechenden und einer reflektierenden, selektiv oder nicht selektiv absorbierenden
- 20 Beschichtung aufweisen. Nachteile dieser Erfindung sind der technisch sehr aufwendige und kostenintensive Herstellungsprozeß sowie die oft schwere Reproduzierbarkeit der Pigmente in der gewünschten Produktqualität.
- 25 Aufgabe der vorliegenden Erfindung ist es, ein im wesentlichen transparentes Interferenzpigment mit kräftigen Interferenzfarben und/oder einer starken Winkelabhängigkeit der Interferenzfarben zur Verfügung zu stellen, das sich durch seine vorteilhaften Anwendungseigenschaften auszeichnet und gleichzeitig auf einfache Art und Weise hergestellt
- 30 werden kann.
- 35 Überraschenderweise wurde nun ein Interferenzpigment auf Basis von mehrfach beschichteten plättchenförmigen Substraten gefunden, das eine bestimmte Anordnung optisch funktioneller Schichten enthält, wodurch besondere optische Effekte erzielt werden.

Gegenstand der Erfindung sind somit Interferenzpigmente auf der Basis von mehrfach beschichteten plättchenförmigen Substraten, die mindestens eine Schichtenfolge aus

- 5 (A) einer Beschichtung mit einem Brechungsindex $n \geq 2,0$,
- (B) einer farblosen Beschichtung mit einem Brechungsindex $n \leq 1,8$, und
- 10 (C) einer nicht absorbierenden hochbrechenden Beschichtung,
- sowie gegebenenfalls
- (D) eine äußere Schutzschicht
- 15 aufweisen.

Gegenstand der Erfindung ist weiterhin die Verwendung der erfindungsgemäßen Pigmente in Farben, Lacken, Druckfarben, Kunststoffen, keramischen Materialien, Gläsern und kosmetischen Formulierungen.

- 20 Geeignete Basissubstrate für die erfindungsgemäßen Mehrschichtpigmente sind einerseits opake und andererseits transparente plättchenförmige Substrate. Bevorzugte Substrate sind Schichtsilikate sowie mit Metalloxiden beschichtete plättchenförmige Materialien. Insbesondere
- 25 geeignet sind natürliche und synthetische Glimmer, Talkum, Kaolin, plättchenförmige Eisenoxide, Bismutoxidchlorid, Glas-, SiO_2 -, Al_2O_3 -, TiO_2 - oder synthetische Keramikflakes, synthetische trägerfreie Plättchen, LCPs oder andere vergleichbare Materialien.

- 30 Die Größe der Basissubstrate ist an sich nicht kritisch und kann auf den jeweiligen Anwendungszweck abgestimmt werden. In der Regel haben die plättchenförmigen Substrate eine Dicke zwischen 0,1 und 5 μm , insbesondere zwischen 0,2 und 4,5 μm . Die Ausdehnung in den beiden anderen Bereichen beträgt üblicherweise zwischen 1 und 250 μm ,
- 35 vorzugsweise zwischen 2 und 200 μm und insbesondere zwischen 5 und 50 μm .

Die Dicke der einzelnen Schichten mit hohem und niedrigem Brechungsindex auf dem Basissubstrat ist wesentlich für die optischen Eigenschaften des Pigments. Für ein Pigment mit intensiven Interferenzfarben, muß die Dicke der einzelnen Schichten genau aufeinander eingestellt werden.

5

Wenn n der Brechungsindex einer dünnen Schicht und d ihre Dicke ist, wird die Interferenzfarbe dieser Schicht von dem Produkt $n \cdot d$ ($n \cdot d$ = optische Dicke) bestimmt. Die bei Normallichteinfall im reflektierten Licht entstehenden Farben eines solchen Films ergeben sich aus einer

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Verstärkung des Lichtes der Wellenlänge

$$\lambda = \frac{4}{2N-1} \cdot n \cdot d$$

15

und durch Schwächung des Lichtes der Wellenlänge,

$$\lambda = \frac{2}{N} \cdot n \cdot d$$

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wobei N eine positive ganze Zahl ist.

25

Die bei zunehmender Filmdicke resultierende Variation der Farbe ergibt sich aus der Verstärkung bzw. Schwächung bestimmter Wellenlängen des Lichtes durch Interferenz. Wenn mehrere Schichten in einem Mehrschichtpigment die gleiche optische Dicke besitzen, wird die Farbe des reflektierten Lichts mit zunehmender Zahl der Schichten intensiver. Darüber hinaus kann durch geeignete Wahl der Schichtdicken eine besonders starke Variation der Farbe in Abhängigkeit vom Betrachtungswinkel erreicht werden. Es bildet sich ein ausgeprägter sogenannter Farbflop aus. Die Dicke der einzelnen Metalloxidschichten unabhängig von ihrem Brechungsindex beträgt in Abhängigkeit vom Anwendungsgebiet in der Regel 10 bis 1000 nm, vorzugsweise 15 bis 800 nm und insbesondere 20-600 nm.

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Die erfindungsgemäßen Glanzpigmente weisen eine hochbrechende Beschichtung (A) in Kombination mit einer farblosen niedrigbrechenden Beschichtung (B) und einer darauf befindlichen nicht absorbierenden hochbrechenden Beschichtung auf. Die Pigmente können mehrere,
5 gleiche oder verschiedene Kombinationen an Schichtpaketen enthalten, bevorzugt ist aber die Belegung des Substrats mit nur einem Schichtpaket (A) + (B) + (C). Zur Intensivierung des Farbflops kann das erfindungsgemäße Pigment bis zu 4 Schichtpakete enthalten, wobei die Dicke aller Schichten auf dem Substrat 3 µm allerdings nicht überschreiten sollte.

10 Die hochbrechende Schicht (A) hat einen Brechungsindex $n \geq 2,0$, vorzugsweise $n \geq 2,1$. Als Schichtmaterial (A) eignen sich alle dem Fachmann bekannten hochbrechenden Materialien, die filmartig und dauerhaft auf die Substratteilchen aufgebracht werden können. Besonders
15 geeignet sind Metalloxide oder Metalloxidgemische, wie z.B. TiO_2 , Fe_2O_3 , ZrO_2 , ZnO , SnO_2 , oder Verbindungen mit hoher Brechzahl, wie z.B. Eisentitanate, Eisenoxidhydrate, Titansuboxide, Chromoxid, Bismutvanadat, Cobaltaluminat sowie Mischungen bzw. Mischphasen der genannten Verbindungen untereinander oder mit anderen Metalloxiden.

20 Die Dicke der Schicht (A) beträgt 10 - 550 nm, vorzugsweise 15 - 400 nm und insbesondere 20 - 350 nm.

25 Als farblose niedrigbrechende für die Beschichtung (B) geeignete Materialien sind vorzugsweise Metalloxide bzw. die entsprechenden Oxidhydrate, wie z.B. SiO_2 , Al_2O_3 , $\text{AlO}(\text{OH})$, B_2O_3 oder ein Gemisch der genannten Metalloxide, geeignet. Die Dicke der Schicht (B) beträgt 10 - 1000 nm, vorzugsweise 20 - 800 nm und insbesondere 30 - 600 nm.

30 Für die nicht absorbierende hochbrechende Beschichtung (C) eignen sich insbesondere farblose Metalloxide wie TiO_2 , ZrO_2 , SnO_2 , ZnO und BiOCl sowie deren Gemische. Die Dicke der Schicht (C) beträgt 10 - 550 nm, vorzugsweise 15 - 400 nm und insbesondere 20 - 350 nm.

35 Neben dem Standardschichtpaket (A) + (B) + (C), das das erfindungsgemäße Pigment bis zu viermal aufweisen kann, gibt es weitere

bevorzugte Ausführungsformen. So kann das erfindungsgemäße Pigment zwischen dem Substrat (S) und der Schicht (A), zwischen der Schicht (A) und (B), der Schicht (B) und (C) und/oder der Schicht (C) und der Deckschicht (D) eine weitere absorbierende oder nicht absorbierende Schicht [(S1), (A1), (B1), (C1)] aufweisen. Die Dicken der Zwischenschichten betragen 1 - 50 nm, vorzugsweise 1 - 40 nm und insbesondere 1 - 30 nm.

Eine besonders bevorzugte Ausführungsform ist die Beschichtung des Substrats mit folgendem Schichtpaket:

- (S1) optional, SnO_2
- (A) TiO_2 oder Fe_2O_3
- (B) SiO_2
- (B1) optional, SnO_2
- (C) TiO_2
- (D) anwendungsbezogene Nachbeschichtung

Durch die Beschichtung der Substrate mit hochbrechenden Schichten (A) und (C) und einer niedrigbrechenden Schicht (B) und gegebenenfalls weiteren farbigen oder farblosen Beschichtungen entstehen Pigmente, deren Farbe, Glanz, Deckvermögen und Winkelabhängigkeit des Farbeindrucks in weiten Grenzen variiert werden können.

Die erfindungsgemäßen Pigmente lassen sich leicht herstellen durch die Erzeugung mehrerer hoch und niedrig brechender Interferenzschichten mit genau definierter Dicke und glatter Oberfläche auf den feinteiligen, plättchenförmigen Substraten.

Die Metalloxidschichten werden vorzugsweise naßchemisch aufgebracht, wobei die zur Herstellung von Perlglanzpigmenten entwickelten naßchemischen Beschichtungsverfahren angewendet werden können; derartige Verfahren sind z.B. beschrieben in DE 14 67 468, DE 19 59 988, DE 20 09 566, DE 22 14 545, DE 22 15 191, DE 22 44 298, DE 23 13 331, DE 25 22 572, DE 31 37 808, DE 31 37 809, DE 31 51 343, DE 31 51 354, DE 31 51 355, DE 32 11 602, DE 32 35 017 oder auch in weiteren Patentdokumenten und sonstigen Publikationen.

Bei der Naßbeschichtung werden die Substratpartikel in Wasser suspendiert und mit einem oder mehreren hydrolysierbaren Metallsalzen bei einem für die Hydrolyse geeigneten pH-Wert versetzt, der so gewählt wird, daß die Metalloxide bzw. Metalloxidhydrate direkt auf den Plättchen ausgefällt werden, ohne daß es zu Nebenfällungen kommt. Der pH-Wert wird üblicherweise durch gleichzeitiges Zudosieren einer Base und/oder Säure konstant gehalten. Anschließend werden die Pigmente abgetrennt, gewaschen und getrocknet und gegebenenfalls geglüht, wobei die Glüh-
temperatur im Hinblick auf die jeweils vorliegende Beschichtung optimiert werden kann. In der Regel liegen die Glühtemperaturen zwischen 250 und 1000 °C, vorzugsweise zwischen 350 und 900 °C. Falls gewünscht können die Pigmente nach Aufbringen einzelner Beschichtungen abgetrennt, getrocknet und ggf. geglüht werden, um dann zur Auffällung der weiteren Schichten wieder resuspendiert zu werden.

Weiterhin kann die Beschichtung auch in einem Wirbelbettreaktor durch Gasphasenbeschichtung erfolgen, wobei z.B. die in EP 0 045 851 und EP 0 106 235 zur Herstellung von Perlglanzpigmenten vorgeschlagenen Verfahren entsprechend angewendet werden können.

Als Metalloxid mit einem hohen Brechungsindex wird bevorzugt Titandioxid und/oder Eisenoxid und als Metalloxid mit niedrigem Brechungsindex Siliziumdioxid verwendet.

Für das Aufbringen der Titandioxidschichten wird das im US 3,553,001 beschriebene Verfahren bevorzugt.

Zu einer auf etwa 50-100 °C erhitzten Suspension des zu beschichtenden Materials wird langsam eine wäßrige Titansalzlösung zugegeben, und es wird durch gleichzeitiges Zudosieren einer Base, wie z.B. wäßrige Ammoniaklösung oder wäßrige Alkalilauge, ein weitgehend konstanter pH-Wert von etwa 0,5-5 eingehalten. Sobald die gewünschte Schichtdicke der TiO₂-Fällung erreicht ist, wird die Zugabe der Titansalzlösung und der Base gestoppt.

- 5 Dieses, auch als Titrationsverfahren bezeichnete Verfahren zeichnet sich dadurch aus, daß ein Überschuß an Titansalz vermieden wird. Das wird dadurch erreicht, daß man pro Zeiteinheit nur eine solche Menge der Hydrolyse zuführt, wie sie für eine gleichmäßige Beschichtung mit dem hydratisierten TiO_2 erforderlich ist und wie pro Zeiteinheit von der verfügbaren Oberfläche der zu beschichtenden Teilchen aufgenommen werden kann. Es entstehen deshalb keine hydratisierten Titandioxidteilchen, die nicht auf der zu beschichtenden Oberfläche niedergeschlagen sind.
- 10 Das Aufbringen der Siliziumdioxidschichten kann z. B. wie folgt vorgenommen werden. Zu einer auf etwa 50-100 °C erhitzten Suspension des zu beschichtenden Substrats wird eine Kali- oder Natronwasserglaslösung, zudosiert. Durch gleichzeitige Zugabe einer verdünnten Mineralsäure, wie z. B. HCl , HNO_3 oder H_2SO_4 , wird der pH-Wert bei ca. 6 - 9
- 15 konstant gehalten. Sobald die gewünschte Schichtdicke an SiO_2 erreicht ist, wird die Zugabe der Wasserglaslösung gestoppt. Anschließend wird ca. 0,5 h nachgerührt.
- 20 Zur Erhöhung der Licht- und Wetterstabilität empfiehlt es sich häufig, in Abhängigkeit vom Einsatzgebiet das fertige Pigment einer Nachbeschichtung oder Nachbehandlung zu unterziehen. Als Nachbeschichtungen bzw. Nachbehandlungen kommen beispielsweise die in den DE-PS 22 15 191, DE-OS 31 51 354, DE-OS 32 35 017 oder DE-OS 33 34 598 beschriebenen Verfahren in Frage. Durch diese
- 25 Nachbeschichtung wird die chemische Stabilität weiter erhöht oder die Handhabung des Pigments, insbesondere die Einarbeitung in unterschiedliche Medien, erleichtert.
- 30 Die erfindungsgemäßen Pigmente sind mit einer Vielzahl von Farbsystemen kompatibel vorzugsweise aus dem Bereich der Lacke, Farben und Druckfarben, insbesondere Sicherheitsdruckfarben. Aufgrund der nicht kopierbaren optischen Effekte können die erfindungsgemäßen Pigmente insbesondere bei der Herstellung von fälschungssicheren Wertschriften, wie z. B. Geldscheine, Schecks, Scheckkarten, Kredit-
- 35 karten, Ausweisen, etc., verwendet werden. Ferner sind die Pigmente

auch für die Lasermarkierung von Papier und Kunststoffen sowie für Anwendungen im Agrarbereich, z.B. für Gewächshausfolien, geeignet.

5 Gegenstand der Erfindung ist somit auch die Verwendung der Pigmente in Formulierungen wie Farben, Druckfarben, Lacken, Kunststoffen, keramischen Materialien, Gläsern und zur Kosmetikpräparation.

10 Es versteht sich von selbst, daß für die verschiedenen Anwendungszwecke die Mehrschichtpigmente auch vorteilhaft in Abmischung mit anderen Pigmenten, wie z. B. transparenten und deckenden Weiß-, Bunt- und Schwarzpigmenten sowie mit plättchenförmigen Eisenoxiden, organischen Pigmenten, holographischen Pigmenten, LCPs (Liquid Crystal Polymers), und herkömmlichen transparenten, bunten und schwarzen Glanzpigmenten auf der Basis von metalloxidbeschichteten Glimmer- und
15 SiO_2 -Plättchen, etc., verwendet werden können. Die Mehrschichtpigmente können in jedem Verhältnis mit handelsüblichen Pigmenten und Füllern gemischt werden.

20 Die nachfolgenden Beispiele sollen die Erfindung näher erläutern ohne sie jedoch zu beschränken.

Beispiele

Beispiel 1

25 100 g Glimmer (PSD 10-60 μm) werden in 2 l vollentsalztem Wasser auf 80 °C erhitzt. Bei dieser Temperatur werden unter kräftigem Rühren 430 g Eisen-III-chlorid-Lösung (14,25 % Fe) zudosiert. Dabei wird mit Natronlauge (32 % NaOH) der pH-Wert konstant bei 4,0 gehalten. Anschließend
30 wird der pH-Wert mit Salzsäure (15 % HCl) auf 1,8 abgesenkt und bei diesem pH-Wert 30 ml TiCl_4 -Lösung (400 g TiCl_4 /l) zugegeben. Der pH-Wert wird dabei mit Natronlauge (32 % NaOH) konstant gehalten. Anschließend wird der pH-Wert mit Natronlauge (32 % NaOH) auf 7,5 angehoben und bei diesem pH eine Lösung von 252 g Natronwasserglas
35 (27 % SiO_2) in 252 g vollentsalztem Wasser zugegeben. Der pH-Wert wird dabei mit Salzsäure (15 % HCl) konstant gehalten.

5 Danach wird der pH-Wert mit Salzsäure (15 % HCl) auf 2,0 abgesenkt und bei diesem pH-Wert eine Lösung von 3 g $\text{SnCl}_4 \times 5 \text{H}_2\text{O}$ und 10 ml Salzsäure (37 % HCl) in 90 ml vollentsalztem Wasser zudosiert. Der pH-Wert wird dabei mit Natronlauge (32 % NaOH) konstant gehalten. Anschließend wird der pH-Wert mit Salzsäure (15 % HCl) auf 1,8 abgesenkt und bei diesem pH-Wert 655 ml TiCl_4 -Lösung (400 g/l) zudosiert. Dabei wird der pH-Wert mit Natronlauge (32 % NaOH) konstant gehalten. Nach Zugabe der TiCl_4 -Lösung wird 15 Min. nachgerührt und das Produkt abfiltriert, mit vollentsalztem Wasser gewaschen, bei ca. 110 °C getrocknet und 45 Min. bei 850 °C geglüht. Das erhaltene Interferenzpigment zeichnet sich durch eine intensive rotviolette Interferenzfarbe aus.

Beispiel 2

15 100 g Glimmer (PSD 10-60 μm) werden in 2 l vollentsalztem Wasser auf 80 °C erhitzt. Bei dieser Temperatur werden unter kräftigem Rühren 430 g Eisen-III-chlorid-Lösung (14,25 % Fe) zudosiert. Dabei wird mit Natronlauge (32 % NaOH) der pH-Wert konstant bei 4,0 gehalten. Anschließend wird der pH-Wert mit Natronlauge (32 % NaOH) auf 7,5 angehoben und bei diesem pH eine Lösung von 252 g Natronwasserglas (27 % SiO_2) in 252 g vollentsalztem Wasser zugegeben. Der pH-Wert wird dabei mit Salzsäure (15 % HCl) konstant gehalten.

25 Danach wird der pH-Wert mit Salzsäure (15 % HCl) auf 2,0 abgesenkt und eine Lösung von 3 g $\text{SnCl}_4 \times 5 \text{H}_2\text{O}$ und 10 ml Salzsäure (37 % HCl) in 90 ml vollentsalztem Wasser zudosiert. Der pH-Wert wird dabei mit Natronlauge (32 % NaOH) konstant gehalten. Anschließend wird der pH-Wert mit Salzsäure (15 % HCl) auf 1,8 abgesenkt und 476 ml TiCl_4 -Lösung (400 g/l) zudosiert. Dabei wird der pH-Wert mit Natronlauge (32 % NaOH) konstant gehalten. Nach Zugabe der TiCl_4 -Lösung wird 15 Min. nachgerührt und das Produkt abfiltriert, mit vollentsalztem Wasser gewaschen, bei 110 °C getrocknet und 30 Min. bei 850 °C geglüht. Das erhaltene Interferenzpigment zeichnet sich durch eine intensive rote Interferenzfarbe aus.

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Beispiel 3

100 g Muskovit-Glimmer (Teilchengröße 10-60 μm) werden in 2 l voll-
entsalztem Wasser auf 80 °C erwärmt. Unter kräftigem Rühren wird dann
5 eine Lösung von 3 g $\text{SnCl}_4 \times 5 \text{H}_2\text{O}$ und 10 ml Salzsäure (37 % HCl) in
90 ml vollentsalztem Wasser bei pH 2,0 zugegeben. Der pH-Wert wird
dabei mit Natronlauge (32 % NaOH) konstant gehalten. Anschließend
werden bei pH 1,8 155 ml TiCl_4 -Lösung (400 g/ TiCl_4 /l) zugegeben. Der pH-
Wert wird dabei mit Natronlauge (32 % NaOH) konstant gehalten. Darauf-
10 hin wird der pH-Wert mit Natronlauge auf 2,6 erhöht und bei diesem pH-
Wert 100 ml einer Lösung von 25 ml TiCl_4 -Lösung (400 g TiCl_4 /l), 48 g
 FeCl_3 -Lösung (14,25 % Fe) und 4,8 g $\text{AlCl}_3 \times 6 \text{H}_2\text{O}$ in vollentsalztem
Wasser zugegeben. Dabei wird der pH-Wert mit Natronlauge (32 %
NaOH) konstant gehalten.

15 Anschließend wird der pH-Wert mit Natronlauge (32 % NaOH) auf 7,5
erhöht und bei diesem pH-Wert eine Lösung von 271 g Natronwasserglas
(27 % SiO_2) in 271 g vollentsalztem Wasser zudosiert. Der pH-Wert wird
mit Salzsäure (10 % HCl) konstant gehalten. Anschließend wird der pH-
20 Wert mit Salzsäure (10 % HCl) auf 2,0 abgesenkt und eine Lösung von 3 g
 $\text{SnCl}_4 \times 5 \text{H}_2\text{O}$ und 10 ml Salzsäure (37 % NaOH) in 90 ml VE-Wasser
zudosiert. Der pH-Wert wird dabei mit Natronlauge (32 % NaOH) konstant
gehalten. Anschließend werden bei pH = 1,8 45 ml TiCl_4 -Lösung (400 g
 TiCl_4 /l) zugegeben, wobei der pH-Wert wiederum mit Natronlauge (32 %
25 NaOH) konstant gehalten wird. Danach wird der pH-Wert mit Natronlauge
(32 % NaOH) auf 2,6 erhöht und bei diesem pH-Wert 230 ml einer Lösung
von 129 ml TiCl_4 -Lösung (400 g TiCl_4 /l), 206 g FeCl_3 -Lösung (14,25 % Fe)
und 10,2 g $\text{AlCl}_3 \times 6 \text{H}_2\text{O}$ in 157 ml VE-Wasser zudosiert. Der pH-Wert
wird dabei mit Natronlauge (32 % NaOH) konstant gehalten. Zuletzt wird
30 das Pigment abgesaugt, mit vollentsalztem Wasser gewaschen, bei
110 °C getrocknet und 30 Min. bei 850 °C geglüht. Man erhält ein intensiv
rotviolett gefärbtes Interferenzpigment, das beim Abkippen über orange in
ein kräftiges gelbgrün übergeht.

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Beispiel 4

Das getrocknete Pigment aus Beispiel 2 wird 30 Minuten bei 850 °C in Formiergasatmosphäre (N₂/H₂; 85/15) geglüht. Das auf diesem Wege
5 hergestellte Pigment zeigt einen intensiven Bronzeeffekt und starken Glanz.

Beispiel 5

10 100 g Muskovit-Glimmer (Teilchengröße 10 - 60 µm) werden in 2 l vollentsalztem Wasser auf 80 °C erwärmt. Unter kräftigem Rühren wird dann eine Lösung von 3 g SnCl₄ x 5 H₂O und 10 ml Salzsäure (37 % HCl) in 90 ml vollentsalztem Wasser bei pH 2,0 mit einer Dosierate von
15 4 ml/min. zugegeben. der pH-Wert wird dabei mit Natronlauge (32 % NaOH) konstant gehalten. Anschließend werden bei pH 1,8 155 ml TiCl₄-Lösung (400 g TiCl₄/l) mit einer Dosierate von 2 ml/min. zugegeben. Der pH-Wert wird dabei mit Natronlauge (32 % NaOH) konstant gehalten.
Daraufhin wird der pH-Wert mit Natronlauge auf 2,6 erhöht und bei diesem pH 100 ml einer Lösung von 25 ml TiCl₄-Lösung (400 g TiCl₄/l), 48 g FeCl₃-
20 Lösung (14,25 % Fe) und 4,8 g AlCl₃ x 6 H₂O in vollentsalztem Wasser zugegeben. Dabei wird der pH mit Natronlauge (32 % NaOH) konstant gehalten.

Anschließend wird der pH mit Natronlauge (32 % NaOH) auf 7,5 erhöht
25 und bei diesem pH-Wert eine Lösung von 297 g Natronwasserglas (27 % SiO₂) in 297 g vollentsalztem Wasser mit einer Geschwindigkeit von 2 ml/min. zudosiert. Der pH-Wert wird mit Salzsäure (10 % HCl) konstant gehalten. Anschließend wird der pH-Wert mit Salzsäure (10 % HCl) auf 2,0 abgesenkt und eine Lösung von 3 g SnCl₄ x 5 H₂O und 10 ml Salzsäure
30 (37 % HCl) in 90 ml vollentsalztem Wasser mit einer Geschwindigkeit von 4 ml/min. zudosiert. Der pH-Wert wird dabei mit Natronlauge (32 % NaOH) konstant gehalten. Anschließend werden bei pH 1,8 250,5 ml TiCl₄-Lösung (400 g TiCl₄/l) mit einer Geschwindigkeit von 2 ml/min. zugegeben, wobei der pH-Wert wiederum mit Natronlauge (32 % NaOH) konstant gehalten
35 wird.

Anschließend wird das Pigment abgesaugt, mit VE-Wasser gewaschen, bei 110 °C getrocknet. Das erhaltene Pigment besitzt nach dieser Stufe rotviolette Farbe, die beim Abkippen in Gelbgrün übergeht.

- 5 Abschließend wird bei 850 °C 30 Minuten geglüht. Man erhält ein gelbrot glänzendes Interferenzpigment, dessen Farbe beim Abkippen in gelbgrün übergeht.

Beispiel 6

- 10 Die Fällung der Metalloxidschichten wird analog Beispiel 5 durchgeführt. Zusätzlich werden bei pH-Wert 2,6 130 ml einer Mischung von 129 ml TiCl_4 -Lösung (400 g TiCl_4/l), 147 ml FeCl_3 -Lösung (14,08 % Fe), 10,2 g $\text{AlCl}_3 \times 6 \text{ H}_2\text{O}$ und 157 ml vollentsalztem Wasser mit einer Dosierate von 1 ml/min. zugesetzt. Der pH-Wert wird dabei mit Natronlauge (32 % NaOH) konstant gehalten.

Die Aufarbeitung erfolgt wie bei den Beispielen 1 - 5.

- 20 Das getrocknete Pigment zeigt intensive rotviolette Farbe mit hohem Glanz, die beim Abkippen in orange übergeht. Nach Glühung glänzt das Pigment gelbrot, wobei die Farbe beim Abkippen in ein kräftig glänzendes Gelb übergeht.

25 Beispiel 7

- Das getrocknete Produkt aus Beispiel 4 wird 30 Minuten bei 850 °C in Formiergasatmosphäre ($\text{N}_2/\text{H}_2=85/15$) geglüht. Das auf diesem Wege hergestellte Pigment zeigt einen roten Bronzeeffekt und starken Glanz
30 sowie erhöhtes Deckvermögen. Die Farbe geht beim Abkippen in ein kräftiges Gelbgrün über.

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Beispiel 8

5 Das getrocknete Produkt aus Beispiel 5 wird 30 Minuten bei 850 °C in Formiergasatmosphäre ($N_2/H_2=85/15$) geglüht. Das auf diesem Wege hergestellte Pigment zeigt einen tiefroten Bronzeeffekt und starken Glanz sowie erhöhtes Deckvermögen. Die Farbe geht beim Abkippen in ein kräftiges Goldgelb über.

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Patentansprüche

- 5 1. Interferenzpigmente auf der Basis von mehrfach beschichteten
plättchenförmigen Substraten, die mindestens eine Schichtenfolge
aus
- (A) einer Beschichtung mit einem Brechungsindex $n \geq 2,0$,
- 10 (B) einer farblosen Beschichtung mit einem Brechungsindex
 $n \leq 1,8$, und
- (C) einer nicht absorbierenden hochbrechenden Beschichtung,
sowie gegebenenfalls
- 15 (D) eine äußere Schutzschicht
- aufweisen.
- 20 2. Interferenzpigmente nach Anspruch 1, dadurch gekennzeichnet, daß
sich zwischen dem Substrat (S) und der Schicht (A), der Schicht (A)
und (B), der Schicht (B) und (C) und/oder der Schicht (C) und (D)
eine weitere farbige oder farblose Metalloxidschicht (S1), (A1), (B1)
und/oder (C1) befindet.
- 25 3. Interferenzpigmente nach Anspruch 1 oder 2, dadurch gekenn-
zeichnet, daß es sich bei den plättchenförmigen Substraten um
natürlichen oder synthetischen Glimmer, Glas-, Al_2O_3 -, SiO_2 - oder
 TiO_2 -Flakes sowie mit Metalloxiden beschichtete, plättchenförmige
- 30 Materialien handelt.
4. Interferenzpigmente nach einem der Ansprüche 1 bis 3, dadurch
gekennzeichnet, daß die Schichten (A), (B) und (C) im wesentlichen
aus Metalloxiden bestehen.
- 35

5. Interferenzpigmente nach einem der Ansprüche 1 bis 4, dadurch gekennzeichnet, daß die Schicht (A) im wesentlichen aus Titandioxid, Eisenoxid, Bismutoxidchlorid, Zirkonoxid, Zinnoxid, Zinkoxid, Titansuboxiden, Eisentitanaten, Eisenoxidhydraten, Chromoxid, Bismutvanadat, Cobaltaluminat oder deren Gemischen besteht.
6. Interferenzpigmente nach einem der Ansprüche 1 bis 5, dadurch gekennzeichnet, daß die Schicht (B) im wesentlichen aus Siliziumdioxid, Aluminiumoxid, Magnesiumfluorid oder deren Gemischen besteht.
7. Interferenzpigmente nach einem der Ansprüche 1 bis 6, dadurch gekennzeichnet, daß die Schicht (C) im wesentlichen aus Titandioxid, Bismutoxidchlorid, Zirkonoxid, Zinnoxid, Zinkoxid oder deren Gemischen besteht.
8. Interferenzpigmente nach einem der Ansprüche 1 bis 7, dadurch gekennzeichnet, daß sie bis zu viermal die Schichtenfolge (A) - (C) aufweisen.
9. Interferenzpigmente nach Anspruch 8, dadurch gekennzeichnet, daß sie nur eine Schichtenfolge (A) - (C) enthalten.
10. Verfahren zur Herstellung der Interferenzpigmente nach einem der Ansprüche 1 bis 8, dadurch gekennzeichnet, daß die Metalloxide naßchemisch durch hydrolytische Zersetzung von Metallsalzen in wäßrigen Medium auf das plättchenförmige Substrat aufgebracht werden.
11. Verwendung der Interferenzpigmente nach Anspruch 1 in Farben, Lacken, Druckfarben, Kunststoffen, keramischen Materialien, Gläsern und in kosmetischen Formulierungen.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 98/06508

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C09C1/00 C09D7/12 C08K3/00 A61K7/00 C04B33/14
C03C4/02 C09D11/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C09C C09D C08K A61K C04B C03C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 94 01498 A (MERCK PATENT GMBH ; IWASA KAZUHISA (JP); NITTA KATSUHISA (JP); NOGU) 20 January 1994 see the whole document ----	1-7, 10, 11
X	US 4 168 986 A (VENIS JR JOSEPH J) 25 September 1979 see claims 1-19 ----	1
X	US 4 017 326 A (DAVIS CHESTER) 12 April 1977 see claims 1-4 ----	1
P, X	WO 98 12266 A (MERCK PATENT GMBH ; AMBROSIUS KLAUS (DE); DIETZ JOHANN (DE); PARUSE) 26 March 1998 see the whole document ----- -/--	1-11

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

9 February 1999

Date of mailing of the international search report

16/02/1999

Name and mailing address of the ISA

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Authorized officer

LIBBERECHT, E

INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 98/06508

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication where appropriate, of the relevant passages	Relevant to claim No.
X	<p>US 3 767 443 A (CLARK D ET AL)</p> <p>23 October 1973</p> <p>see the whole document</p> <p>-----</p>	1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 98/06508

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9401498 A	20-01-1994	JP 6016964 A EP 0602217 A FI 940977 A US 5456749 A	25-01-1994 22-06-1994 01-03-1994 10-10-1995
US 4168986 A	25-09-1979	NONE	
US 4017326 A	12-04-1977	US 4010293 A US 4184872 A	01-03-1977 22-01-1980
WO 9812266 A	26-03-1998	DE 19638708 A AU 4621197 A CA 2238035 A CZ 9801555 A EP 0882099 A	16-04-1998 14-04-1998 26-03-1998 16-09-1998 09-12-1998
US 3767443 A	23-10-1973	BE 720539 A CH 550237 A DE 1792478 A FR 1581309 A GB 1237866 A NL 6812731 A SE 341227 B US 3627553 A	06-03-1969 14-06-1974 18-11-1971 12-09-1969 30-06-1971 11-03-1969 20-12-1971 14-12-1971

INTERNATIONALER RECHERCHENBERICHT

Internationales Aktenzeichen

PCT/EP 98/06508

A. KLASSIFIZIERUNG DES ANMELDUNGSGEGENSTANDES

IPK 6 C09C1/00 C09D7/12 C08K3/00 A61K7/00 C04B33/14
C03C4/02 C09D11/00

Nach der Internationalen Patentklassifikation (IPK) oder nach der nationalen Klassifikation und der IPK

B. RECHERCHIERTE GEBIETE

Recherchierter Mindestprüfstoff (Klassifikationssystem und Klassifikationssymbole)

IPK 6 C09C C09D C08K A61K C04B C03C

Recherchierte aber nicht zum Mindestprüfstoff gehörende Veröffentlichungen, soweit diese unter die recherchierten Gebiete fallen

Während der internationalen Recherche konsultierte elektronische Datenbank (Name der Datenbank und evtl. verwendete Suchbegriffe)

C. ALS WESENTLICH ANGESEHENE UNTERLAGEN

Kategorie	Bezeichnung der Veröffentlichung, soweit erforderlich unter Angabe der in Betracht kommenden Teile	Betr. Anspruch Nr.
X	WO 94 01498 A (MERCK PATENT GMBH ; IWASA KAZUHISA (JP); NITTA KATSUHISA (JP); NOGU) 20. Januar 1994 siehe das ganze Dokument ---	1-7, 10, 11
X	US 4 168 986 A (VENIS JR JOSEPH J) 25. September 1979 siehe Ansprüche 1-19 ---	1
X	US 4 017 326 A (DAVIS CHESTER) 12. April 1977 siehe Ansprüche 1-4 ---	1
P, X	WO 98 12266 A (MERCK PATENT GMBH ; AMBROSIUS KLAUS (DE); DIETZ JOHANN (DE); PARUSE) 26. März 1998 siehe das ganze Dokument ---	1-11
	-/--	

☒ Weitere Veröffentlichungen sind der Fortsetzung von Feld C zu entnehmen

☒ Siehe Anhang Patentfamilie

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Datum des Abschlusses der internationalen Recherche

9. Februar 1999

Absenddatum des internationalen Recherchenberichts

16/02/1999

Name und Postanschrift der internationalen Recherchenbehörde

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Bevollmächtigter Bediensteter

LIBBERECHT, E

INTERNATIONALER RECHERCHENBERICHT

Internationales Aktenzeichen

PCT/EP 98/06508

C.(Fortsetzung) ALS WESENTLICH ANGESEHENE UNTERLAGEN

Kategorie	Bezeichnung der Veröffentlichung, soweit erforderlich unter Angabe der in Betracht kommenden Teile	Betr. Anspruch Nr.
X	<p>US 3 767 443 A (CLARK D ET AL)</p> <p>23. Oktober 1973</p> <p>siehe das ganze Dokument</p> <p>-----</p>	1

INTERNATIONALER RECHERCHENBERICHT

Angaben zu Veröffentlichungen, die zur selben Patentfamilie gehören

Internationales Aktenzeichen

PCT/EP 98/06508

Im Recherchenbericht angeführtes Patentdokument	Datum der Veröffentlichung	Mitglied(er) der Patentfamilie	Datum der Veröffentlichung
WO 9401498 A	20-01-1994	JP 6016964 A EP 0602217 A FI 940977 A US 5456749 A	25-01-1994 22-06-1994 01-03-1994 10-10-1995
US 4168986 A	25-09-1979	KEINE	
US 4017326 A	12-04-1977	US 4010293 A US 4184872 A	01-03-1977 22-01-1980
WO 9812266 A	26-03-1998	DE 19638708 A AU 4621197 A CA 2238035 A CZ 9801555 A EP 0882099 A	16-04-1998 14-04-1998 26-03-1998 16-09-1998 09-12-1998
US 3767443 A	23-10-1973	BE 720539 A CH 550237 A DE 1792478 A FR 1581309 A GB 1237866 A NL 6812731 A SE 341227 B US 3627553 A	06-03-1969 14-06-1974 18-11-1971 12-09-1969 30-06-1971 11-03-1969 20-12-1971 14-12-1971



US006596070B1

(12) **United States Patent**
Schmidt et al.

(10) **Patent No.:** US 6,596,070 B1
(45) **Date of Patent:** Jul. 22, 2003

(54) **INTERFERENCE PIGMENTS**

(75) **Inventors:** Christoph Schmidt, Kriftel (DE);
Gerhard Pfaff, Münster (DE);
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(73) **Assignee:** Merck Patent Gesellschaft, Darmstadt (DE)

(*) **Notice:** Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.

(21) **Appl. No.:** 09/529,619

(22) **PCT Filed:** Oct. 17, 1998

(86) **PCT No.:** PCT/EP98/06508

§ 371 (c)(1),

(2), (4) **Date:** Apr. 17, 2000

(87) **PCT Pub. No.:** WO99/20695

PCT Pub. Date: Apr. 29, 1999

(30) **Foreign Application Priority Data**

Oct. 17, 1997 (DE) 197 46 067

(51) **Int. Cl.⁷** C04B 14/20; C09C 1/36;
B32B 15/02; B32B 17/02

(52) **U.S. Cl.** 106/417; 106/415; 106/418;
106/436; 106/438; 106/439; 106/442; 428/404

(58) **Field of Search** 106/415, 417,
106/418, 436, 438, 439, 442; 428/404

(56) **References Cited**

U.S. PATENT DOCUMENTS

3,767,443 A 10/1973 Clark et al. 106/291

4,017,326 A 4/1977 Davis 106/291
4,168,986 A 9/1979 Venis, Jr. 106/291
5,573,584 A * 11/1996 Ostertag et al. 106/417
5,624,486 A * 4/1997 Schmid et al. 106/404
5,958,125 A * 9/1999 Schmid et al. 106/417
6,132,873 A * 10/2000 Dietz et al. 428/404
6,156,115 A * 12/2000 Pfaff et al. 106/403
6,238,471 B1 * 5/2001 Vogt et al. 106/417
6,238,472 B1 * 5/2001 Andes et al. 106/430
6,267,810 B1 * 7/2001 Pfaff et al. 106/415
6,280,520 B1 * 8/2001 Andes et al. 106/415
6,284,032 B2 * 9/2001 Andes et al. 106/436
6,500,251 B1 * 12/2002 Andes et al. 106/415

FOREIGN PATENT DOCUMENTS

DE 2215191 * 3/1972
WO 9401498 1/1994
WO 9812266 3/1998

* cited by examiner

Primary Examiner—Mark L. Bell

Assistant Examiner—Patricia L. Hailey

(74) *Attorney, Agent, or Firm*—Millen, White, Zelano & Branigan, P.C.

(57) **ABSTRACT**

The present invention relates to interference pigments on the basis of multiply coated, platelet-shaped substrates which comprise at least one layer sequence comprising

(A) a coating having a refractive index $n \geq 2.0$,

(B) a colorless coating having a refractive index $n \leq 1.8$, and

(C) a nonabsorbing coating of high refractive index, and, if desired,

(D) an external protective layer.

13 Claims, No Drawings

INTERFERENCE PIGMENTS

The present invention relates to interference pigments based on multiply coated platelet-shaped substrates.

Lustre pigments or special-effect pigments are employed in numerous fields in industry, especially in the sector of automotive finishes, in decorative coating, in plastics, in paints, in printing inks and in cosmetic formulations.

Lustre pigments which exhibit an angle-dependent colour change between two or more interference colours have a play of colour which makes them of particular interest for automotive finishes and in connection with counterfeit-protected documents of value. Pigments of this kind on the basis of multiply coated platelet-shaped substrates are known.

Interference pigments consist generally of platelet-shaped substrates with a thickness of from 200 to 1000 nm which are coated with highly refractive metal oxides or metal oxide mixtures with a thickness of from 50 to 300 nm. The optical properties of these pigments are critically determined by the refractive index of the metal oxide layer. In addition to the possibility of using chemical vapour deposition (CVD) or physical vapour deposition (PVD) techniques to prepare metal oxide layers having high densities and so refractive indices that lie close to the optimum, the deposition of metal oxides on finely divided, platelet-shaped substrates is frequently accomplished by titrating aqueous, usually acidic metal salt solutions against sodium hydroxide solution in the presence of a substrate, as described, for example, in DE 14 67 468 and DE 20 09 566.

A disadvantage of the vapour deposition technique is the high costs it entails. For instance, U.S. Pat. No. 4,434,010 discloses a multilayer interference pigment consisting of a central layer of a reflective metal, such as aluminium, and alternating layers of two transparent dielectric materials of high and low refractive index respectively, such as titanium dioxide and silicon dioxide, for example. This multilayer pigment is used preferably for counterfeit-protected securities.

JP H7-759 discloses a multilayer interference pigment with metallic lustre, for which a substrate is coated with alternate layers of titanium dioxide and silicon dioxide. The substrate comprises flakes of aluminium, gold or silver, or of mica or glass, with a coating of metals. The depth effect which is characteristic of and desired for interference pigments, however, cannot be generated. This is because of the total reflection of the light at the metal layer which forms the core. Consequently, the interference effect remains limited to the layers which are located on the metal layer. Furthermore, the lack of transparency of the substrate greatly restricts the diverse possibilities for combination with further pigments in applications-related formulations.

U.S. Pat. No. 3,438,796 and U.S. Pat. No. 5,135,812 describe, for example, metal lustre pigments having a central opaque aluminium film coated on both sides in alternation with dielectric films of low refractive index, such as silicon dioxide or magnesium fluoride, and with partially transparent metal films, such as films of chromium or aluminium, for example. Owing to the preparation process, the central metal film of these pigments is coated only on the top and bottom sides of the platelets, while the side areas constitute broken edges and lie open towards the medium.

DE 44 05 494, DE 44 37 753, DE 195 16 181 and DE 195 15 988 disclose lustre pigments prepared by coating metal platelets, especially aluminium flakes, with metal oxide layers of low refractive index, such as with a silicon dioxide layer, and with non-selectively absorbing metal oxide layers

or metal layers of high refractive index, using CVD or wet-chemical techniques.

Lustre pigments based on metal substrates frequently have good performance properties, including good opacity, but the result on application, such as in the paint, for example, is a "hard" metallic lustre, which is frequently unwanted.

Lustre pigments based on transparent platelet-shaped substrates which do not have this "hard" metallic lustre are the subject of WO 93/12182. Mica flakes are covered with a metal oxide layer of high refractive index, such as TiO_2 , and with a non-selectively absorbing layer. Depending on the thickness of the TiO_2 layer, when viewed straight on these pigments exhibit a particular interference colour which becomes increasingly weaker as the viewing angle becomes more oblique and which finally flips to grey or black. The interference colour does not change, but a decrease is found in the colour saturation.

JP 1992/93206 claims lustre pigments on the basis of glass flakes or mica particles which are covered with an opaque metal layer and with alternating layers of SiO_2 and TiO_2 .

EP 0 753 545 discloses lustre pigments based on multiply coated, nonmetallic, platelet-shaped substrates which are of high refractive index, are at least partially transparent to visible light and have at least one layer assembly comprising a colourless coating of low refractive index and a reflective coating which absorbs selectively or nonselectively. Disadvantages of this invention are the technically very complex and costly preparation process and the frequent difficulty in reproducing the pigments in the desired product quality.

The object of the present invention is to provide an essentially transparent interference pigment having strong interference colours and/or a strong angular dependence of the interference colours which is notable for its advantageous performance properties and which at the same time can be prepared in a simple manner.

Surprisingly, an interference pigment has now been found which is based on multiply coated, platelet-shaped substrates and comprises a particular arrangement of optically functional layers by means of which particular optical effects are achieved.

The invention therefore provides interference pigments on the basis of multiply coated, platelet-shaped substrates which comprise at least one layer sequence comprising

(A) a coating having a refractive index $n \geq 2.0$,

(B) a colourless coating having a refractive index $n \leq 1.8$, and

(C) a nonabsorbing coating of high refractive index,

and, if desired,

(D) an external protective layer.

The invention also provides for the use of the pigments of the invention in paints, lacquers, printing inks, plastics, ceramic materials, glasses and cosmetic formulations.

Suitable base substrates for the multilayer pigments of the invention are firstly opaque and secondly transparent platelet-shaped substances. Preferred substrates are phyllosilicates and metal oxide-coated, platelet-shaped materials. Of particular suitability are natural and synthetic micas, talc, kaolin, platelet-shaped iron oxides, bismuth oxychloride, flakes of glass, SiO_2 , Al_2O_3 or TiO_2 , synthetic ceramic flakes, carrier-free synthetic platelets, I.C.P.s or other comparable materials.

The size of the base substrates per se is not critical and can be matched to the particular target application. In general, the platelet-shaped substrates have a thickness of between 0.1 and 5 μm , in particular between 0.2 and 4.5 μm . The

extent in the two other dimensions is usually between 1 and 250 μm , preferably between 2 and 200 μm and, in particular, between 5 and 50 μm .

The thickness of the individual layers of high and low refractive index on the base substrate is essential for the optical properties of the pigment. For a pigment with intensive interference colours, the thickness of the individual layers must be adjusted precisely with respect to one another.

If n is the refractive index of a thin layer and d its thickness, the interference colour of this layer is defined by the product $n \cdot d$ ($n \cdot d$ = optical thickness). The colours which result from such a film under perpendicular light incidence in reflected light result from an intensification of the light of wavelength

$$\lambda = \frac{4}{2N-1} \cdot n \cdot d$$

and by an attenuation of the light of wavelength

$$\lambda = \frac{2}{N} \cdot n \cdot d$$

where N is a positive integer.

The variation in colour which results with increasing film thickness is a consequence of the intensification or attenuation of certain light wavelengths through interference. If two or more layers in a multilayer pigment possess the same optical thickness, the colour of the reflected light becomes more intense as the number of layers increases. In addition to this, it is possible through an appropriate choice of layer thicknesses to achieve a particularly strong variation of the colour as a function of the viewing angle. A pronounced, so-called colour flop is developed. The thickness of the individual metal oxide layers, irrespective of their refractive index, depends on the field of use and is generally from 10 to 1000 nm, preferably from 15 to 800 nm and, in particular, 20–600 nm.

The lustre pigments of the invention feature a coating (A) of high refractive index in combination with a colourless coating (B) of low refractive index and located thereon a nonabsorbing coating of high refractive index. The pigments can comprise two or more, identical or different combinations of layer assemblies, although preference is given to covering the substrate with only one layer assembly (A)+(B)+(C). In order to make the colour flop more intense the pigment of the invention may comprise up to 4 layer assemblies, although the thickness of all of the layers on the substrate should not exceed 3 μm .

The layer (A) of high refractive index has a refractive index $n \geq 2.0$, preferably $n \geq 2.1$. Materials suitable as the layer material (A) are all materials known to the skilled worker which are of high refractive index, are filmlike and can be applied permanently to the substrate particles. Particularly suitable materials are metal oxides or metal oxide mixtures, such as TiO_2 , Fe_2O_3 , ZrO_2 , ZnO or SnO_2 , or compounds of high refractive index such as, for example, iron titanates, iron oxide hydrates, titanium suboxides, chromium oxide, bismuth vanadate, cobalt aluminate, and also mixtures or mixed phases of these compounds with one another or with other metal oxides.

The thickness of the layer (A) is 10–550 nm, preferably 15–400 nm and, in particular, 20–350 nm.

Colourless materials of low refractive index suitable for the coating (B) are preferably metal oxides or the corresponding oxide hydrates, such as SiO_2 , Al_2O_3 , $\text{AlO}(\text{OH})$,

B_2O_3 or a mixture of these metal oxides. The thickness of the layer (B) is 10–1000 nm, preferably 20–800 nm and, in particular, 30–600 nm.

Materials particularly suitable for the non-absorbing coating (C) of high refractive index are colourless metal oxides such as TiO_2 , ZrO_2 , SnO_2 , ZnO and BiOCl , and also mixtures thereof. The thickness of the layer (C) is 10–550 nm, preferably 15–400 nm and, in particular, 20–350 nm.

In addition to the standard layer assembly (A)+(B)+(C), which may be present up to four times in the pigment of the invention, there are other preferred embodiments. For instance, between the substrate (S) and the layer (A), between the layer (A) and (B), between layer (B) and (C) and/or between layer (C) and the top layer (D) the pigment of the invention may have a further absorbing or nonabsorbing layer [(S1), (A1), (B1), (C1)]. The thickness of the interlayers is 1–50 nm, preferably 1–40 nm and, in particular, 1–30 nm.

A particularly preferred embodiment is the coating of the substrate with the following layer assembly:

- (S1) optional, SnO_2
- (A) TiO_2 or Fe_2O_3
- (B) SiO_2
- (B1) optional, SnO_2
- (C) TiO_2

- (D) final coating related to application

Coating the substrates with layers (A) and (C) of high refractive index, a layer (B) of low refractive index and, if desired, further coloured or colourless coatings produces pigments whose colour, gloss, opacity and angular dependence of perceived colour can be varied within wide limits.

The pigments of the invention are easy to produce by virtue of the generation of two or more interference layers of high and low refractive index, precisely defined thickness and smooth surface on the finely divided, platelet-shaped substrates.

The metal oxide layers are preferably applied by wet-chemical means, it being possible to use the wet-chemical coating techniques developed for the production of pearl lustre pigments; techniques of this kind are described, for example, in DE 14 67 468, DE 19 59 988, DE 20 09 566, DE 22 14 545, DE 22 15 191, DE 22 44 298, DE 23 13 331, DE 25 22 572, DE 31 37 808, DE 31 37 809, DE 31 51 343, DE 31 51 354, DE 31 51 355, DE 32 11 602, DE 32 35 017 or else in further patent documents and other publications.

In the case of wet coating, the substrate particles are suspended in water, and one or more hydrolysable metal salts are added at a pH which is appropriate for hydrolysis and is chosen such that the metal oxides or metal oxide hydrates are precipitated directly onto the platelets without any instances of secondary precipitation. The pH is kept constant usually by simultaneous metered addition of a base and/or acid. Subsequently, the pigments are separated off, washed and dried and, if desired, are calcined, it being possible to optimize the calcination temperature in respect of the particular coating present. In general, the calcination temperatures are between 250 and 1000° C., preferably between 350 and 900° C. If desired, following the application of individual coatings the pigments can be separated off, dried and, if desired, calcined before being resuspended for the application of further layers by precipitation.

Coating can also take place in a fluidized-bed reactor by means of gas-phase coating, in which case it is possible, for example, to make appropriate use of the techniques proposed in EP 0 045 851 and EP 0 106 235 for preparing pearl lustre pigments.

The metal oxide of high refractive index used is preferably titanium dioxide and/or iron oxide, and the metal oxide of low refractive index preferably used is silicon dioxide.

For the application of the titanium dioxide layers, preference is given to the technique described in U.S. Pat. No. 3,553,001.

An aqueous titanium salt solution is added slowly to a suspension, heated to about 50–100° C., of the material to be coated, and a substantially constant pH of about 0.5–5 is maintained by simultaneous metered addition of a base, for example aqueous ammonia solution or aqueous alkali metal hydroxide solution. As soon as the desired layer thickness of the TiO₂ precipitate has been reached, the addition of both titanium salt solution and base is terminated.

This technique, also referred to as the titration process, is notable for the fact that it avoids an excess of titanium salt. This is achieved by supplying to the hydrolysis only that quantity per unit time which is necessary for uniform coating with the hydrated TiO₂ and which can be received per unit time by the available surface area of the particles to be coated. There is therefore no production of hydrated titanium dioxide particles not precipitated on the surface to be coated.

The application of the silicon dioxide layers can be performed, for example, as follows. A potassium or sodium silicate solution is metered into a suspension, heated to about 50–100° C., of the substrate that is to be coated. The pH is held constant at about 6–9 by simultaneous addition of a dilute mineral acid, such as HCl, HNO₃ or H₂SO₄. As soon as the desired layer thickness of SiO₂ has been reached, the addition of the silicate solution is terminated. The batch is subsequently stirred for about 0.5 h.

In order to enhance the light stability and weather stability it is frequently advisable to subject the finished pigment to an aftercoating or after-treatment process, depending on the field of use. Suitable such processes are those described, for example, in DE-C 22 15 191, DE-A 31 51 354, DE-A 32 35 017 or DE-A 33 34 598. Such aftercoating further increases the chemical stability or facilitates the handling of the pigment, especially its incorporation into different media.

The pigments of the invention are compatible with a large number of colour systems, preferably from the sector of lacquers, paints and printing inks, especially security printing inks. Owing to the uncopyable optical effects, the pigments of the invention can be used in particular for producing counterfeit-protected documents of value, such as bank notes, cheques, cheque cards, credit cards, identity cards, etc. In addition, the pigments are also suitable for the laser marking of paper and plastics and for applications in the agricultural sector, such as for glasshouse films, for example.

The invention therefore also provides for the use of the pigments in formulations such as paints, printing inks, lacquers, plastics, ceramic materials and glasses and for cosmetics preparations.

It is of course the case that for the various target applications the multilayer pigments can also be employed advantageously in blends with other pigments, examples being transparent and hiding white, coloured and black pigments, and with platelet-shaped iron oxides, organic pigments, holographic pigments, LCPs (liquid crystal polymers) and conventional transparent, coloured and black lustre pigments based on metal oxide-coated mica and SiO₂ platelets, etc. The multilayer pigments can be mixed in any proportion with customary commercial pigments and extenders.

The examples which follow are intended to illustrate the invention yet without placing any limitation on it.

EXAMPLES

Example 1

100 g of mica (PSD 10–60 μm) in 2 l of deionized water are heated to 80° C. At this temperature, 430 g of iron(III)

chloride solution (14.25% Fe) are metered in with vigorous stirring. In the course of this addition, the pH is held constant at 4.0 using aqueous sodium hydroxide solution (32% NaOH). Subsequently, the pH is lowered to 1.8 using hydrochloric acid (15% HCl) and at this pH 30 ml of TiCl₄ solution (400 g TiCl₄/l) are added. The pH during this addition is held constant using aqueous sodium hydroxide solution (32% NaOH). The pH is subsequently raised to 7.5 using aqueous sodium hydroxide solution (32% NaOH) and at this pH a solution of 252 g of sodium silicate (27% SiO₂) in 252 g of deionized water is added. During this addition, the pH is kept constant using hydrochloric acid (15% HCl).

Subsequently, the pH is lowered to 2.0 using hydrochloric acid (15% HCl) and at this pH a solution of 3 g of SnCl₄·5H₂O and 10 ml of hydrochloric acid (37% HCl) in 90 ml of deionized water is metered in. During this addition the pH is kept constant using aqueous sodium hydroxide solution (32% NaOH). The pH is subsequently lowered to 1.8 using hydrochloric acid (15% HCl) and at this pH 655 ml of TiCl₄ solution (400 g/l) are metered in. During this addition the pH is kept constant using aqueous sodium hydroxide solution (32% NaOH). Following the addition of the TiCl₄ solution the mixture is stirred for 15 minutes and the product is filtered off, washed with deionized water, dried at about 110° C. and calcined at 850° C. for 45 minutes. The interference pigment obtained has an intense reddish violet interference colour.

Example 2

100 g of mica (PSD 10–60 μm) in 2 l of deionized water are heated to 80° C. At this temperature, 430 g of iron(III) chloride solution (14.25% Fe) are metered in with vigorous stirring. In the course of this addition, the pH is held constant at 4.0 using aqueous sodium hydroxide solution (32% NaOH). The pH is subsequently raised to 7.5 using aqueous sodium hydroxide solution (32% NaOH) and at this pH a solution of 252 g of sodium silicate (27% SiO₂) in 252 g of deionized water is added. During this addition, the pH is kept constant using hydrochloric acid (15% HCl).

Subsequently, the pH is lowered to 2.0 using hydrochloric acid (15% HCl), and a solution of 3 g of SnCl₄·5H₂O and 10 ml of hydrochloric acid (37% HCl) in 90 ml of deionized water is metered in. During this addition the pH is kept constant using aqueous sodium hydroxide solution (32% NaOH). The pH is subsequently lowered to 1.8 using hydrochloric acid (15% HCl), and 476 ml of TiCl₄ solution (400 g/l) are metered in. During this addition the pH is kept constant using aqueous sodium hydroxide solution (32% NaOH). Following the addition of the TiCl₄ solution the mixture is stirred for 15 minutes and the product is filtered off, washed with deionized water, dried at 110° C. and calcined at 850° C. for 30 minutes. The interference pigment obtained has an intense red interference colour.

Example 3

100 g of muscovite mica (particle size 10–60 μm) in 2 l of deionized water are heated to 80° C. Then, with vigorous stirring, a solution of 3 g of SnCl₄·5H₂O and 10 ml of hydrochloric acid (37% HCl) in 90 ml deionized water is added at a pH of 2.0. During this addition the pH is kept constant using aqueous sodium hydroxide solution (32% NaOH). Subsequently, at a pH of 1.8, 155 ml of TiCl₄ solution (400 g TiCl₄/l) are added. During this addition the pH is kept constant using aqueous sodium hydroxide solution (32% NaOH). The pH is subsequently raised to 2.6 using aqueous sodium hydroxide solution and at this pH 100

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ml of a solution of 25 ml of TiCl_4 solution (400 g TiCl_4/l), 48 g of FeCl_3 solution (14.25% Fe) and 4.8 g of $\text{AlCl}_3 \times 6\text{H}_2\text{O}$ in deionized water are added. During this addition the pH is kept constant using aqueous sodium hydroxide solution (32% NaOH).

The pH is subsequently raised to 7.5 using aqueous sodium hydroxide solution (32% NaOH) and at this pH a solution of 271 g of sodium silicate (27% SiO_2) in 271 g of deionized water is metered in. The pH is kept constant using hydrochloric acid (10% HCl). The pH is subsequently lowered to 2.0 using hydrochloric acid (10% HCl), and a solution of 3 g of $\text{SnCl}_4 \times 5\text{H}_2\text{O}$ and 10 ml of hydrochloric acid (37% HCl) in 90 ml of deionized water is metered in. During this addition the pH is kept constant using aqueous sodium hydroxide solution (50% NaOH). Subsequently, at a pH of 1.8, 45 ml of TiCl_4 solution (400 g TiCl_4/l) are added, the pH again being kept constant using aqueous sodium hydroxide solution (32% NaOH). Thereafter the pH is raised to 2.6 using aqueous sodium hydroxide solution (32% NaOH) and at this pH 230 ml of a solution of 129 ml of TiCl_4 solution (400 g TiCl_4/l), 206 g of FeCl_3 solution (14.25% Fe) and 10.2 g $\text{AlCl}_3 \times 6\text{H}_2\text{O}$ in 157 ml of deionized water are metered in. During this addition the pH is kept constant using aqueous sodium hydroxide solution (32% NaOH). Finally the pigment is filtered off with suction, washed with deionized water, dried at 110° C. and calcined at 850° C. for 30 minutes. The result is an interference pigment with an intense reddish violet colour which flips through orange to a strong yellowish green.

Example 4

The dried pigment from Example 2 is calcined at 850° C. for 30 minutes in a forming-gas atmosphere (N_2/H_2 ; 85/15). The pigment prepared in this way exhibits an intense bronze effect and a strong lustre.

Example 5

100 g of muscovite mica (particle size 10–60 μm) in 2 l of deionized water are heated to 80° C. Then, with vigorous stirring, a solution of 3 g of $\text{SnCl}_4 \times 5\text{H}_2\text{O}$ and 10 ml of hydrochloric acid (37% HCl) in 90 ml deionized water is added at a metering rate of 4 ml/min at a pH of 2.0. During this addition the pH is kept constant using aqueous sodium hydroxide solution (32% NaOH). Subsequently, at a pH of 1.8, 155 ml of TiCl_4 solution (400 g TiCl_4/l) are added at a metering rate of 2 ml/min. During this addition the pH is kept constant using aqueous sodium hydroxide solution (32% NaOH). The pH is subsequently raised to 2.6 using aqueous sodium hydroxide solution and at this pH 100 ml of a solution of 25 ml of TiCl_4 solution (400 g TiCl_4/l), 48 g of FeCl_3 solution (14.25% Fe) and 4.8 g of $\text{AlCl}_3 \times 6\text{H}_2\text{O}$ in deionized water are added. During this addition the pH is kept constant using aqueous sodium hydroxide solution (32% NaOH).

The pH is subsequently raised to 7.5 using aqueous sodium hydroxide solution (32% NaOH) and at this pH a solution of 297 g of sodium silicate (27% SiO_2) in 297 g of deionized water is metered in at a rate of 2 ml/min. The pH is kept constant using hydrochloric acid (10% HCl). The pH is subsequently lowered to 2.0 using hydrochloric acid (10% HCl), and a solution of 3 g of $\text{SnCl}_4 \times 5\text{H}_2\text{O}$ and 10 ml of hydrochloric acid (37% HCl) in 90 ml of deionized water is metered in at a rate of 4 ml/min. During this addition the pH is kept constant using aqueous sodium hydroxide solution (32% NaOH). Subsequently, at a pH of 1.8, 250.5 ml of TiCl_4 solution (400 g TiCl_4/l) are added at a rate of 2 ml/min,

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the pH again being kept constant using aqueous sodium hydroxide solution (32% NaOH).

Subsequently the pigment is filtered off with suction, washed with deionized water and dried at 110° C. Following this stage the pigment obtained has a reddish violet colour which flips to yellowish green.

Finally, the pigment is calcined at 850° C. for 30 minutes. The result is an interference pigment with a yellowish red lustre whose colour flips to a yellowish green.

Example 6

The metal oxide layers are precipitated as in Example 5. In addition, at a pH of 2.6, 130 ml of a mixture of 129 ml of TiCl_4 solution (400 g TiCl_4/l) 147 ml of FeCl_3 solution (14.08% Fe), 10.2 g of $\text{AlCl}_3 \times 6\text{H}_2\text{O}$ and 157 ml of deionized water are added at a metering rate of 1 ml/min. During this addition the pH is kept constant using aqueous sodium hydroxide solution (32% NaOH).

The pigment is worked up as in Examples 1–5.

The dried pigment exhibits an intense reddish violet colour of high lustre, which flips to orange. After calcination, the pigment has a yellowish red lustre, with the colour flipping to a strongly lustrous yellow.

Example 7

The dried product from Example 4 is calcined at 850° C. for 30 minutes in a forming-gas atmosphere (N_2/H_2 ; 85/15). The pigment prepared in this way exhibits a red bronze effect and strong lustre and also heightened opacity. On flipping, the colour changes to a strong yellowish green.

Example 8

The dried product from Example 5 is calcined at 850° C. for 30 minutes in a forming-gas atmosphere (N_2/H_2 ; 85/15). The pigment prepared in this way exhibits a deep red bronze effect and strong lustre and also heightened opacity. On flipping, the colour changes to a strong golden yellow.

What is claimed is:

1. An interference pigment comprising a multiply coated, platelet-shaped substrate (S) having at least one layer sequence comprising

(A) a coating having a refractive index $n > 2.0$,

(B) a colourless coating having a refractive index $n > 1.8$, and

(C) a nonabsorbing coating of high refractive index.

2. The interference pigment according to claim 1, wherein between the substrate (S) and the layer (A), the layer (A) and (B), and/or the layer (B) and (C) there is a further colored or colorless metal oxide layer (S1), (A1), (B1) and/or (C1).

3. The interference pigment according to claim 1, wherein the platelet-shaped substrate is natural or synthetic mica, glass, Al_2O_3 , SiO_2 or TiO_2 flakes, or a platelet-shaped material coated with at least one metal oxide.

4. The interference pigment according to claim 1, wherein the layers (A), (B) and (C) consist essentially of metal oxides.

5. The interference pigment according to claim 1, wherein the layer (A) consists essentially of titanium dioxide, iron oxide, bismuth oxychloride, zirconium oxide, tin oxide, zinc oxide, titanium suboxides, iron titanates, iron oxide hydrates, chromium oxide, bismuth vanadate, cobalt aluminate or a mixture thereof.

6. The interference pigment according to claim 1, wherein the layer (B) consists essentially of silicon dioxide, aluminum oxide, magnesium fluoride or a mixture thereof.

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7. The interference pigment according to claim 1, wherein the layer (C) consist essentially of titanium dioxide, bismuth oxychloride, zirconium oxide, tin oxide, zinc oxide or a mixture thereof.

8. The interference pigment according to claim 1, having the layer sequence (A)–(C) up to four times.

9. The interference pigment according to claim 8, containing only one layer sequence (A)–(C).

10. A process for preparing an interference pigment according to claim 1, comprising applying the metal oxides wet-chemically to the platelet-shaped substrate by hydrolytic decomposition of metal salts in an aqueous medium.

11. A paint, lacquer, printing ink, plastic, ceramic material, glass or cosmetic formulation, comprising an interference pigment according to claim 1.

12. The interference pigment according to claim 1, further comprising (D) an external protective layer.

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13. An interference pigment comprising a multiply coated, platelet-shaped substrate having at least one layer sequence comprising

(A) a coating having a refractive index $n > 2.0$, selected from the group consisting of iron oxide, bismuth oxychloride, zirconium oxide, bismuth vanadate, cobalt aluminate or a mixture thereof,

(B) a colourless coating having a refractive index $n > 1.8$, selected from the group consisting of titanium dioxide, tin oxide, zinc oxide or a mixture thereof,

(C) a nonabsorbing coating of high refractive index, and,

(D) an external protective layer.

* * * * *

Angle-Dependent Optical Effects Deriving from Submicron Structures of Films and Pigments

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Received July 6, 1998 (Revised Manuscript Received March 15, 1999)

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I. Introduction

A. General Introduction

Angle-dependent optical effects can be found in various industrial products and consequently in

different end-user applications. These effects are used for functional purposes, such as security printing and optical filters, and for decorative purposes, as in cosmetics and car paints.

In the security field, the user takes advantage of the fact that the angle-dependent optical effect cannot be easily copied with conventional copier machines or photographic techniques. Forging is only possible if similar products are utilized, which makes forging much more complicated and expensive. Consequently, pearlescent and optical multilayer pigments are used on bank notes by many countries.

Multilayer films or films containing pearlescent pigments reflect a certain portion of the visible light. Therefore, they are increasingly being used in greenhouse applications to influence the light that shines onto the plants and, hence, influences their growth.

In the decorative applications, three major advantages are seen from the use of angle-dependent optical effects. The first is the illusion of optical depth, which is, for example, created by the gradual angle-dependent color changes observed of pearlescent pigments in car paints. This illusion is especially strong when extended areas are profiled as in automotive fenders. Pearlescent pigments can be found in the lacquers of more than 40% of the cars in the United States and 30% in Europe.

The second advantage is the subtle to startling eye-catching effect of an angle-depending color. A consequence of this is that pearlescent pigments are often used in packaging for their aesthetic and promotional eye-catching appeal. The third field is the ability to imitate the effect of natural pearls in buttons, plastic bottles, and many other objects.

B. Scope of the Review

Angle-dependent optical effects can be achieved by using extended films, for example, wrapping paper; extended coatings, for example, glass dip coatings; or coatings that contain special effect pigments.

In this review, a special focus is set on the angle-dependent optical effects found in particles, e.g., pigments, because they can be used in a broader set of applications than extended optical films and coatings. Similar products are used for functional purposes, for example, conductive pigments. These are not a subject of this review.



Gerhard Pfaff was born in Meiningen, Germany, in 1953. He received his diploma in chemistry (1978) and Ph.D. (with A. Feltz) from the Friedrich-Schiller-University of Jena (1983). His postgraduate research was in the field of solid-state chemistry and ceramic materials at the University of Jena. He was a postdoctoral fellow at the C.N.R.S. Institute of Solid-State Chemistry of Bordeaux, France (with J. P. Bonnet), in 1987. In 1991, he joined Merck KGaA, Darmstadt, Germany, as a research manager in the R&D department of the Pigments Division. Since 1994, he has been the head of product development for effect pigments in this division. In 1997, he received the habilitation in the field of inorganic chemistry at the Technical University of Darmstadt (with R. Kniep), where he is now also a lecturer. His research interests include synthesis, structural investigation, and application behavior of effect pigments, materials with advanced optical and electrical properties, and perovskites.



Peter Reynders was born in Bad Gandersheim, Germany, in 1958. He received his diploma in organic chemistry from the University of Göttingen (1984) and his doctoral degree in physical chemistry at the Max Planck Institute of Biophysical Chemistry, Göttingen, Germany (1988). In the following years, he worked in the field of industrial nanochemistry at Lucent Bell Laboratories, NJ. He is currently Research Manager in the Pigments Division at Merck KGaA, Darmstadt, Germany. His research interests include the synthesis, sintering, and characterization of nanocrystalline oxides and surface modification and coloristics of industrial pigments.

II. Theory of Angle-Dependent Optical Effects

Due to the importance of interference pigments and films, the theory of interference colors is presented below. The background of dichroism and holographic effects is discussed together with the products.

A. Interference at Single Layers

The physical background of optical interference effects has been the subject of many publications.¹ The literature, however, deals either with the theory for idealized thin films²⁻⁵ or with the measurement

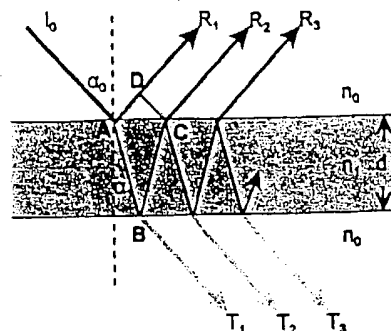


Figure 1. Splitting of a light beam at a thin layer. Reflections occur at both interfaces of the film.

and characterization of pearlescent pigments in application media.^{5,6} A theory for interference pigments that includes the optical effects of the particles boundaries is not yet developed.

When a beam of white light strikes a thin film with a thickness on the order of the wavelength of visible light, interference colors can be detected. The color observed depends on the viewing angle.

The basis of the interference theory is the Fresnel equations, which give the amplitudes r of reflected electromagnetic waves as

$$\begin{aligned} r_s &= \frac{n_0 \cos \alpha_0 - n_1 \cos \alpha_1}{n_0 \cos \alpha_0 + n_1 \cos \alpha_1} \\ r_p &= \frac{n_1 \cos \alpha_1 - n_0 \cos \alpha_0}{n_1 \cos \alpha_1 + n_0 \cos \alpha_0} \end{aligned} \quad (1)$$

n_0 and n_1 are the refractive indices of the two media. The indices S and P refer to the orientation of the electromagnetic field vector relative to the plane of incidence: perpendicular = S-polarized light, parallel = P-polarized light.

The intensity R of the light is closely related to its amplitude

$$\begin{aligned} R_s &= r_s^2 \\ R_p &= r_p^2 \end{aligned} \quad (2)$$

The geometry of the light pathway within the two media conforms to Snell's law (eq 3) and the reflection law that the incident angle is equal to the reflecting angle. According to these terms, an incident light

$$n_0 \sin \alpha_0 = n_1 \sin \alpha_1 \quad (3)$$

beam of intensity I_0 and amplitude A_0 splits up into reflected and a transmitted portions, see Figure 1. The amplitudes R_i of the reflected light beams coming from single and multiple reflections can be calculated using the Fresnel equations

$$\begin{aligned} R_1 &= r_1^2 A_0^2 \\ R_2 &= t_1^2 r_2^2 A_0^2 \\ R_3 &= t_1^2 r_1^2 r_2^2 A_0^2, \text{ etc.} \end{aligned} \quad (4)$$

with t as the amplitude of the transmitted light. The

reflection at the upper and lower surfaces gives rise to different pathways of the particular beams. This difference of the traversed distances, G , is represented by the following terms, see Figure 1

$$G = 2n_1 \overline{AB} - n_0 \overline{AD} \quad (5)$$

Combined with Snell's law (eq 3), the angle-dependent form is obtained

$$G = 2n_1 d \sqrt{1 - \frac{n_0^2}{n_1^2} \sin^2 \alpha_0} \quad (6)$$

The phase difference angle δ follows as

$$\delta = \frac{2\pi}{\lambda} G = \frac{4\pi n_1 d}{\lambda} \sqrt{1 - \frac{n_0^2}{n_1^2} \sin^2 \alpha_0} \quad (7)$$

The superposition of the reflected beams must be performed for amplitude and phase, see eq 4

$$\begin{aligned} R &= R_1 + R_2 + R_3 + \dots \\ &= r_1 + t_1^2 r_2 e^{-i\delta} - t_1^2 r_1 r_2^2 e^{-2i\delta} + t_1^2 r_1^2 r_2^3 e^{-3i\delta} - \dots \\ &= r_1 + t_1^2 r_2 e^{-i\delta} (1 - r_1 r_2 e^{-i\delta} + r_1^2 r_2^2 e^{-2i\delta} - \\ &\quad r_1^3 r_2^3 e^{-3i\delta} + \dots) \quad (8) \end{aligned}$$

This geometrical series can be transformed to

$$R = r_1 + \frac{t_1^2 r_2 e^{-i\delta}}{1 + r_1 r_2 e^{-i\delta}} \quad (9)$$

The optical impression for the human eye is directly related to the reflected light intensity I_r , which is obtained by multiplication of R with its conjugated complex value.

For nonabsorbing media ($r^2 + t^2 = 1$; $I_r + I_t = I_0$) and using eq 7, we obtain the following expression for the intensity of the reflected light I_r

$$I_r = \frac{r_1^2 + r_2^2 + 2r_1 r_2 \cos \delta}{1 + r_1^2 r_2^2 + 2r_1 r_2 \cos \delta} \quad (10)$$

and for the intensity of the transmitted light I_t

$$I_t = \frac{(1 - r_1^2)(1 - r_2^2)}{1 + r_1^2 r_2^2 + 2r_1 r_2 \cos \delta} \quad (11)$$

For a thin film in a homogeneous medium we can set $r_1 = -r_2 = r$ and obtain

$$R = \frac{1 - \cos \delta}{\frac{1 + r^4}{2r^2} - \cos \delta} \quad (12)$$

When the incident angle is variable, the amplitude

Table 1. Refractive Indices n_D of Important Transparent Coating Materials

substance	refractive index n_D (550 nm)	max reflected intensity of thin layer (%)	
		in air	in Lacquer of $n_D = 1.5$
glass	1.5	15	0
natural muscovite	1.58	18	0
Al ₂ O ₃ corundum	1.77	27	3
natural pearl essence	1.91 (perpendicular) 1.78 (parallel)	32	6
basic lead carbonate	2.0	36	8
BiOCl	2.15	42	12
TiO ₂ anatase	2.3	47	16
TiO ₂ rutile	2.7	58	28

r has to be replaced by the Fresnel expressions of r_s and r_p (eq 1). In the case of perpendicular incidence of light, these equations collapse to

$$r_s = r_p = \frac{n_0 - n_1}{n_0 + n_1} \quad (13)$$

In eq 12, the reflected light intensity R reaches a maximum value for $\cos \delta = -1$. This is realized for distinctive wavelengths and distinctive optical film thicknesses $n_1 d$

$$\lambda_{\max} = \frac{4n_1 d}{2m + 1} \text{ for } m = 0, 1, 2, 3, \dots$$

$$n_1 d = (2m + 1) \frac{\lambda_{\max}}{4} \quad (14)$$

At these wavelengths we observe the maximum reflection R which exclusively depends on the refractive index n_1 of the platelet according to

$$R = \left(\frac{n_1^2 - n_0^2}{n_1^2 + n_0^2} \right)^2 \quad (15)$$

This is the well-known equation for maximum reflectance of perpendicular incidence on a thin film. Values for the refractive index of the most important coating materials are shown in Table 1.

If the refractive index of the thin film is higher than that of the medium, which is normally the case, a phase shift of 180° occurs for the portion of the light which is reflected at the upper surface of the film. This phase shift is already taken into account by eq 1.

According to eq 11, R is extinguished for $\cos \delta = +1$. The condition for this is

$$\lambda_{\min} = \frac{4n_1 d}{2m} \text{ for } m = 1, 2, 3, \dots$$

$$n_1 d = m \frac{\lambda_{\min}}{2} \quad (16)$$

For eqs 13–16, we have restricted the model to perpendicular incidence. If this restriction is lifted,

Table 2. Current Producers of Oxidic Effect Pigments (1998)^a

company	product range	remarks
Merck KGaA (in the U. S.: EM Industries)	full range of metal oxide/mica pigments, pearlescent pigments on silica and alumina flakes, BiOCl	
Engelhard Corporation	full range of metal oxide/mica pigments, BiOCl, natural pearl essence, basic lead carbonate	bought pearlescent pigment business from Mearl in 1996 and from Semo in 1997
BASF	metal oxide/aluminum pigments, limited range of metal oxide/mica, produced by CVD	
Eckart Werke	limited range of metal oxide/mica pigments, metallic pigments	bought pearlescent pigment business from Kemira in 1998
Flex Products	multilayer pigments by CVD, mainly for security printing	subsidiary of OCLI
ISP Van Dyk	BiOCl	formerly Mallinckrodt
Shiseido	titanium suboxide/mica	
Sudarshan	limited range of metal oxide/mica pigments	partly owned by Dainippon Ink

^a There are some smaller producers that cover approximately less than 2% of the world market.

the relation of the interference color with the incident and viewing angle α makes the equations more complicated, due to the angle dependence of the phase difference δ . Equation 16 then becomes

$$\lambda_{\max} = \frac{4n_1d}{2m+1} \sqrt{1 - \frac{n_0^2}{n_1^2} \sin^2 \alpha}$$

for $m = 0, 1, 2, 3, \dots$ (17)

This equation shows that the maximum reflectance shifts to a shorter wavelength when the viewing angle is increased. A thin film illuminated by white light can, for example, show traveling colors from red to blue when the observer changes his position toward a flatter viewing angle. A flatter viewing angle corresponds to a longer path through the layers or, respectively, an increased layer thickness. Figure 2 shows the reflectivity spectra of a series of pearlescent pigments consisting of mica platelets with increasing rutile layer thicknesses.

From eq 17 it is also seen that a broader distribution of the thickness d would lead to a less defined color and could finally wipe out the interference maximum. This is the case for ground natural mica which is used as a substrate for the production of pearlescent pigments, see below. It consists of platelets whose thickness vary from particle to particle, typically in the range of 100–1000 nm. Therefore, the single mica particles show interference colors but not the ensemble of particles.¹ In contrast to mica, the alumina and silica substrates mentioned below have a constant thickness and show interference colors. This is also the case for bismuth oxychloride and basic lead carbonate pigments.

The optical layers can also be built up by materials that absorb light such as iron oxides or chromium oxides. In this case, the mass tone is combined with the angle-dependent interference color. For the calculation of the optical characteristics of such layers, the real refractive index in the equations above is replaced by the complex refractive index $n_i = n - ik$, where k is the extinction coefficient, which is of course also a function of the wavelength of the incident light.

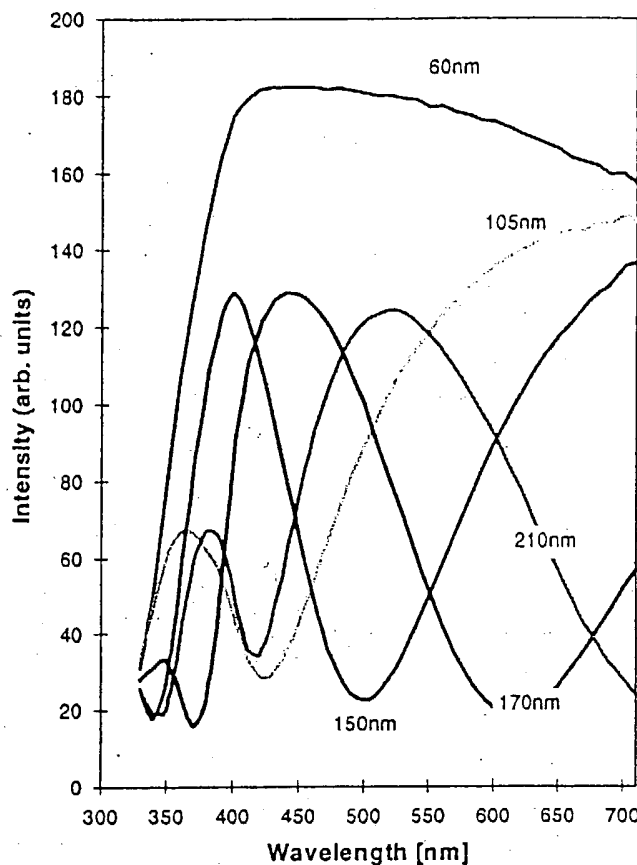


Figure 2. Reflectivity of pigmented nitrocellulose lacquer films containing commercial mica-based pearlescent pigments with rutile layers of various thicknesses indicated in the figure: 60 nm corresponds to a silverwhite, 105 nm to a golden, 150 nm to a red, 170 nm to a blue, and 210 nm to a green interference color.

B. Interference at Multiple Layers

When several thin films of different refractive indices are combined, multiple reflections occur.⁷ As a consequence, stronger and better defined interference colors can be achieved, see Figure 9. This multilayer technique is found in nature as the deep iridescent colors of beetles exocuticles,⁸ butterfly wings, bird feathers,⁹ and plants¹⁰ as well as the nacreous appearance of natural pearls and sea shells.¹¹ The well-known TiO_2 -mica pigments consist of a three-layer system, as shown in Figure 3. Every pigment particle shows the stronger interference color of a three-layer TiO_2 -mica- TiO_2 system. How-

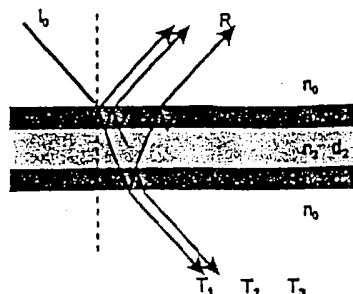


Figure 3. Splitting of a light beam at a three-layer system. Multiple reflections occur at the various interfaces.

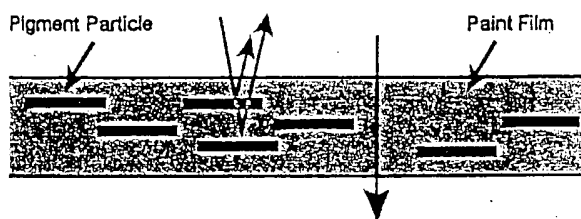


Figure 4. General scheme of platelet-shaped pigment particles in a paint film. Typical thicknesses of the film are between 5 (offset printing), 30 (automotive coatings), and 120 μm (powder coatings). The mean thickness of the pigment particles is about 0.5 μm .

ever, due to the broad thickness distribution of the mica platelets, the ensemble of particles has nearly the same optical characteristics as a single TiO_2 layer on mica.¹ New pearlescent pigments based on synthetic substrates are true three-layer systems and show, therefore, an improved appearance, see below.

If materials are used with a smaller difference in the refractive indices, it becomes necessary to use many more layers to achieve a reasonable interference effect. There are commercial products which are based on organic polymers such as polystyrene and polyethylene and consist of up to 1000 layers.¹²

The interference color effects of multilayer films cannot be calculated in a simple way. It would go beyond the scope of this review to show the theoretical background; therefore, it is referred to in the literature.^{13,14} However, as for the single layer, the intensity of the reflected light depends strongly on the differences between the refractive indices.

C. Basic Requirements for Pearlescent Pigments

Pearlescent pigments must fulfill many requirements to be successful in the market place. First of all, they should show a strong pearlescent effect. As outlined above, a high difference in the refractive indices is essential for this goal. The choice of coating materials is limited to, for example, titanium oxides,

iron oxides, and chromium oxides and the choice of substrates to silicon dioxide, silicates, and aluminum oxide. The layers of the coating material should also be as dense as possible to avoid the "dilution" of their refractive index, see eq 18 below. The materials used should also be environmentally safe and globally approved for the use in the field of the desired application.

Since the pearlescent effect is a directed reflection, unfavorable diffuse reflection should be reduced to a minimum to suppress a milky diffuse background. This means that, for example, side precipitation during the coating process and crack formation in the coating layer during calcination should be avoided. The edges of plate-shaped particles also give rise to diffuse light scattering. As a consequence, larger particle surface dimensions (diameters) lead to stronger pearlescent effects as the edge scattering effect is greatly reduced. However, the single pigment particles become distinguishable by the naked eye when their diameter reaches 60 μm , and the effect changes from a silky to a sparkle appearance. This is generally not desired for car paints and cosmetics, although there are applications for the sparkle effect like snowboards and toothpastes. Typical particle diameter fractions are in the range of 0–15, 5–25, and 10–40 μm .

The pigment substrate (core), e.g., mica, acts as a mechanical support and is often necessary as a template for the synthesis of the high-refractive layers, which will be discussed below. However, if the substrate particles have a wide thickness distribution, they become optically inactive as shown above¹ and dilute the optical effect. In this case, the substrate should be as thin as possible but still thick enough to be mechanically stable. Typical mean values of mica substrate thicknesses are in the range of 200–600 nm.

D. Computer-Aided Simulations and Their Limitations

Computer programs are commercially available for calculation of the optical appearance of monolayer, multilayer, and absorbing systems.¹⁵ They give excellent results for nonabsorbing continuous dense layers which were, for example, produced by physical or chemical vapor deposition (PVD, CVD). For the calculation it has to be kept in mind that the refractive index depends on the wavelength of the incident light, an effect that is particularly strong for titanium dioxide. Often calculation of absorbing layers does not agree well with the practical measurements. The reason is that the extinction coef-

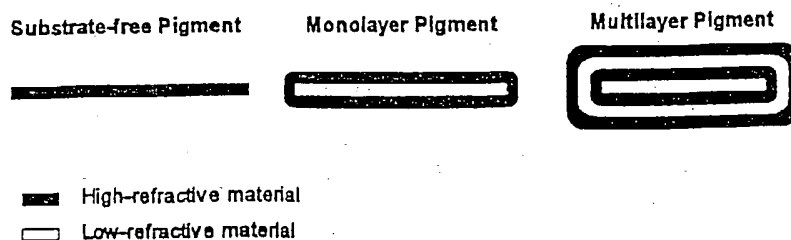


Figure 5. General scheme of substrate-free, monolayer, and multilayer pigments.

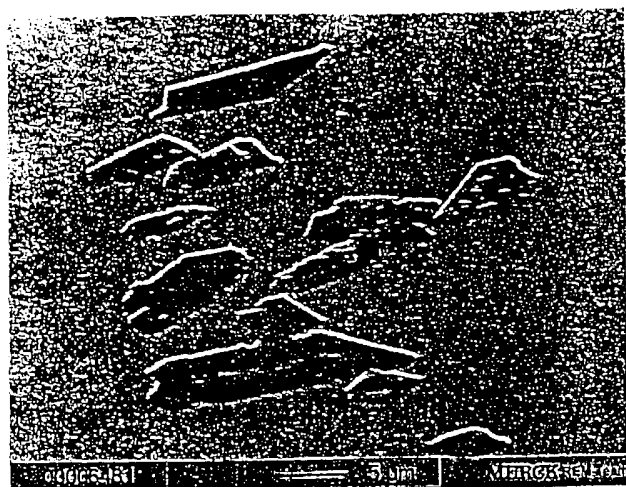


Figure 6. SEM photo of pigment particles isolated from natural pearl essence (fishsilver).

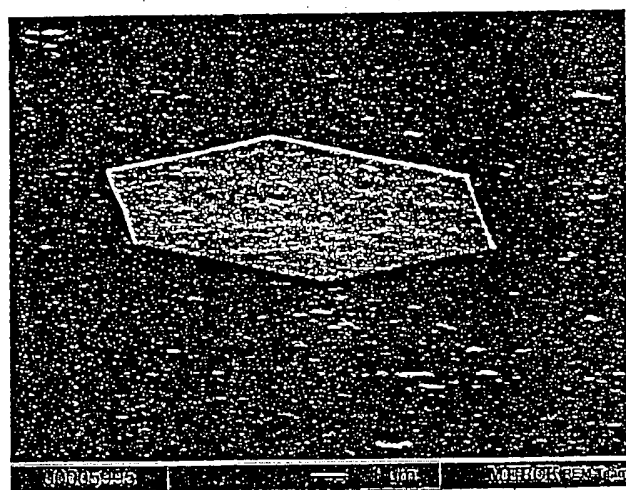


Figure 7. SEM photo of a basic lead carbonate pigment particle with a thickness of 46 nm and a yellow interference color.

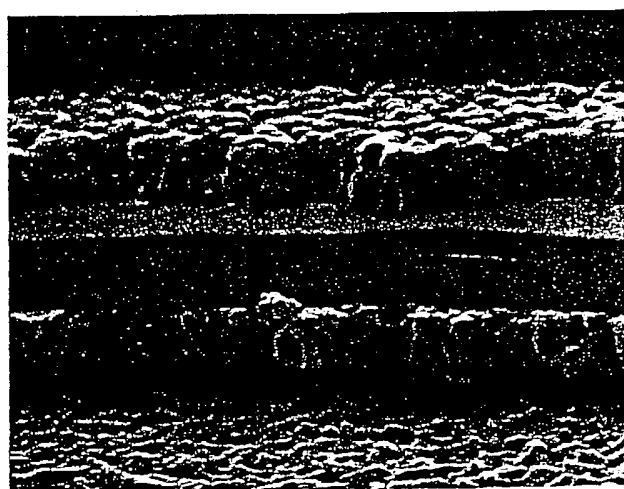


Figure 8. SEM photo of a cross-section through an anatase/mica pigment particle. The anatase layers are precipitated to yield an average thickness of 140 nm on each side of the mica substrate for a blue interference color.

ficient of all light-absorbing layers, e.g., iron oxides and chromium oxides, depends strongly on the grain size, grain shape, dopants, impurities, and preparation.¹⁶

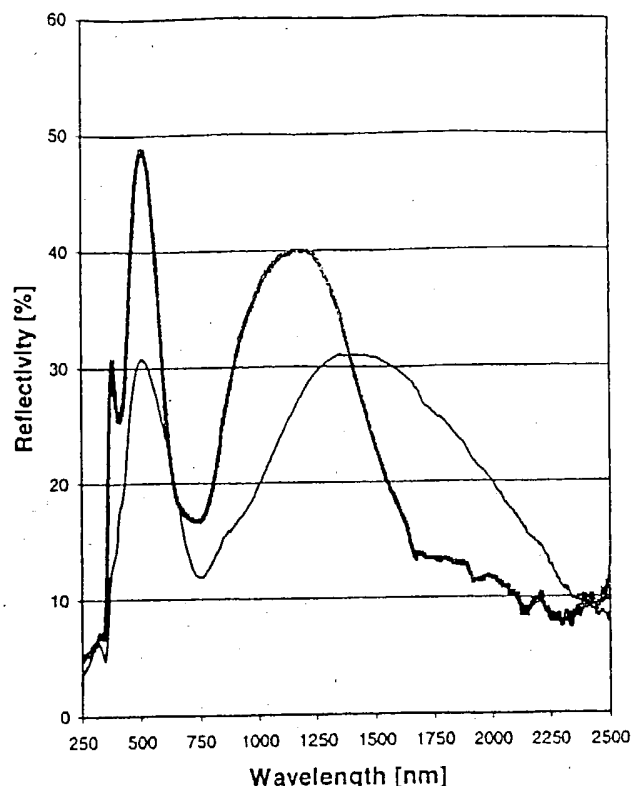


Figure 9. Total reflectivity of two green interference pigments consisting of mica flakes coated with a single layer of 160 nm anatase (thin line), respectively, a three-layer system of 160 nm anatase, 85 nm SiO_2 , and 160 nm anatase (bold curve) (see Figure 4). The thickness distribution of the mica flakes is broad enough to decouple the top and bottom coatings.¹ Measurements were carried out on nitrocellulose lacquer films, containing approximately 2 wt % pigment in an Ullbricht integration sphere.

Real systems show a porosity in the optical layers that "dilutes" the bulk refractive index, yielding an effective refractive index of the film. This can be taken into account by using the so-called Lorentz-Lorenz or Clausius-Mosotti equation¹⁷

$$\frac{n_f^2 - 1}{n_f^2 + 2} = \frac{n_m^2 - 1}{n_m^2 + 2}P + \frac{n_w^2 - 1}{n_w^2 + 2}\alpha(1 - P) \quad (18)$$

where n_f = the effective refractive index of the film, n_m = the refractive index of the bulk, n_w = the refractive index of the material filling the pores, α = the relative proportion of pores filled with said material, and P = the film packing density (relative density).

The porosity of TiO_2 films has been extensively investigated.¹⁸ Liquid-phase or gas-phase deposition leads to a significant porosity, often more than 25% of the layer. Dense layers can only be prepared using high-energy ion plating techniques. The porosity leads to a reduction of the reflected light intensity, which can be calculated by putting the effective refractive index from eq 18 into eq 15. The Lorentz-Lorenz equation also explains the fact that interference pigment powders show an unusual shift of the interference color when their pores are filled with small amounts of liquid such as water or lacquer.

However, there are limitations due to the fact that the calculation does not take into account the particle

characteristics of a pigment. First, the edges of the pigment particles lead to diffuse scattering, resulting in the addition of a diffuse background to the optical spectra. Second, in a typical application, for example, a lacquer coating, the pigment particles do not cover the whole area, see Figure 4. Third, there is also a contribution to the reflection from particles that lie underneath, see Figure 4, leading to a higher reflection intensity. Fourth, the alignment of the platelets could not be optimal, leading to a less pronounced angle-dependence of the reflection. A good parallel alignment is often achieved by the flow characteristics of the platelets themselves, due to their high aspect ratios. The thickness reduction during drying of a lacquer film normally leads to a good orientation. However, when the random orientation of the pigment particles is quenched by high-viscosity or ultrafast curing or when the structure is disturbed by excessive media shrinkage or pigment agglomeration, the parallel orientation of the pigment platelets can be less pronounced.

III. Extended Interference Films

Extended films were the subject of a short review published in 1992.¹⁹

A. Inorganic Films by Gas-Phase Deposition

Angle-dependent optical effects can also be generated on flat surfaces using evaporation techniques. Commercially used methods are (1) high-vacuum evaporation, also with electron guns,²⁰ (2) physical deposition processes such as magnetron sputtering, ion plating, ion-assisted evaporation,²¹ (3) chemical vapor deposition (CVD) such as low-pressure CVD and plasma-enhanced CVD.²²

Since most of the substrates, such as glass, show a low refractive index, the coating must possess a higher refractive index than the substrate. It normally consists of titania or zirconia. ZnS and Ta₂O₅ are also used. Very often multilayer coatings are applied that contain SiO₂, Al₂O₃, or MgF₂ as low-refractive layers next to the high-refractive materials and optional transparent or semitransparent metal layers. Mixed oxide layers are also feasible as long as the evaporation is consecutive. Very often small amounts of doping material reduce crystallization and increase, therefore, the homogeneity of the films.

Because of cost considerations these types of processes are only used for optical lenses, filters, laser mirrors, eyeglasses, and communication. Of increasing importance are nonclassical coatings such as electrochromic and transparent conductive coatings.

B. Inorganic Films by Liquid-Phase Deposition

Extended optical layers are very often generated from the liquid phase. The following methods can be used: (1) dipping processes, for large surfaces, the most economical and easily applicable; (2) spreading out the liquid film by centrifugally spinning the wetted surfaces (spin-coating), only applicable for small circular objects; (3) spraying processes.

To produce homogeneous layers, the coating solutions must have the following characteristics: (1) adequate solubility of the initial compounds, and a minimal tendency toward crystallization during the evaporation of the solvent; (2) sufficiently small contact angles between substrate and solution to obtain a good wetting; (3) easy transformation of the deposited gel film into a solid homogeneous film layer without the appearance of cracks or hazing.

The liquid-phase preparation as well as the optical effects of the resulting films have been well-known for some decades and are covered by an older review article.²³ The liquid-phase deposition processes are today widely used for glass coatings.

Reversible electrochromic and photochromic effects have been observed with thin films made of WO₃, SnO₂ and TiO₂.²⁴

C. Organic Films

Angle-dependent optical effects can be generated by organic multilayer films.²⁵ Because the refractive indices of organic materials differ much less than those of inorganics, such films usually contain more than 70 layers, sometimes even up to 1000 layers to achieve a strong interference effect. The difference of the refractive indices should be, nevertheless, at least 0.06.

The individual layers are normally 50–400 nm thick. As outlined in the theoretical part above, the quantity of the reflected light and the chroma²⁶ depends on the difference of refractive indices, the number of layers, the ratio of the optical thicknesses of the layers, and the uniformity of the thicknesses.²⁷

The multilayer organic films can be produced by a chill-roll casting technique using a conventional single manifold flat film in combination with a feedblock that collects the melts from two or more extruders (co-extrusion) and arranges them into the desired layer design. The low-refractive index polymer is usually polymethacrylate, polymethacrylate-polyester, polypropylene, ethylene vinyl acetate, or polyether glycol (all having n_D of 1.48–1.50). The high-refractive index polymer is often chosen to be poly(ethylene terephthalate) and poly(butylene terephthalate) and their copolymers (1.55–1.61), polystyrene (1.60), or polycarbonate (1.59). The organic films can contain colorants and/or pigments.²⁸

At the moment it is not possible to achieve a uniform interference color throughout the whole film. The production process generates a slight thickness variation leading to different color patches, for example, green and blue, that appear very close to each other. Therefore, these films are not widely used with the exception of gift wrapping materials.

IV. Pearlescent Pigments

Special effect pigments with angle-dependent optical effects have a growing economic significance. The total worldwide annual market volume is about 15 000 tons for metallic and 14 000 tons for oxidic pigments.²⁹ Pigments can be produced by synthesis of pigment particles or by grinding a film that already shows the angle-dependent optical effects.

The field of pearlescent pigments has been reviewed in 1988 by L. M. Greenstein³ and in 1992 in *Ullmann's Encyclopedia of Industrial Chemistry*.²⁹ There is also a book³⁰ about pearlescent pigments which covers marketing and popular aspects and a book about special effect pigments and their applications.³¹

Pearlescent pigments can be grouped into two fields: (1) particles that consist of basically one optically homogeneous material; (2) particles that have a layered structure on a substrate, see Figure 5. Substrate-free pigments can be single crystals such as BiOCl or polycrystalline flakes such as TiO₂ flakes, see below. Their optical thickness is often chosen to be on the order of one-fourth of the wavelength of visible light so that the interference color is at its maximum and the absorption is as low as possible. However, this means that they are often very thin. Therefore, the mechanical stability is usually lower than for substrate-based pigments.

Only a few substances can be forced to crystallize as thin platelets. Therefore, thin platelets are used as so-called substrates or templates onto which materials of high refractive index can be precipitated. The best known examples are the pearlescent pigments that are based on TiO₂ precipitated onto platelets of natural mica, see below. Pigments based on transparent substrates, such as the mica-based products, can be easily combined with absorption pigments even in thicker coatings. They create the impression of optical depth due to their smooth and gradual change of reflection and/or chroma. On the other side, pigments with metallic substrates have advantages in very thin coatings due to their strong hiding power. Mixtures of mica pigments and metallic pigments are often used in car paints.³²

For outdoor use, especially for car paints and architectural applications, the chemical and photochemical reactivity of the metal-oxide-containing pigments is normally reduced by an additional treatment.³³

A. Substrate-Free Pigments

1. Natural Pearl Essence

Natural pearls and nacreous shells have been used since ancient times for decorative purposes. In 1656, the French rosary maker Jaquin isolated a silky lustrous suspension from fish scales and produced the first pearlescent pigments.³⁴ This suspension is often called natural pearl essence. The pigment particles are platelet-shaped with a very high aspect ratio (0.05 μm \times 1–10 μm \times 20–50 μm , see Figure 6) and consist of 75–97% guanine and 3–25% hypoxanthine.³⁵

To date there is no commercial synthetic process for producing similar platelet-shaped products of such brilliance. One is, therefore, limited to a process based on the natural supply: An aqueous suspension of white fish scales is treated with organic solvents in a complicated washing and phase-transfer process to remove proteins and irregular guanine crystals.³⁶ One ton of fish yields less than 250 g of guanine. The pigment particles show a high tendency to agglomerate and are, therefore, only handled as dispersions.

Natural pearl essence is very expensive but shows some advantages over synthetic pearlescent pigments: it shows a high but soft luster ($n_D = 1.79$ (parallel) to 1.91 (perpendicular)). It is not brittle and has a relatively low density of 1.6 g/cm³, which reduces settling in liquid formulations. It is almost exclusively used in expensive cosmetic applications.³⁷ The world production of natural pearl essence in 1998 is estimated to be well under 50 t.

2. Basic Lead Carbonate

The first commercially successful synthetic pearlescent pigments were hexagonal lead salt crystals, especially basic lead carbonate Pb(OH)₂·2PbCO₃. Basic lead carbonate^{3,38} is precipitated from aqueous lead acetate with carbon dioxide under carefully controlled reaction conditions. The resulting platelets are less than 0.05 μm thick and show hexagonal dimensions of about 20 μm , yielding an aspect ratio of >200, see Figure 7. Due to their high refractive index of 2.0 and their even surface, they exhibit a very strong luster. If the thickness of the platelets is increased by slightly modified reaction conditions, interference colors can be obtained.

The crystals are very fragile and are handled only in dispersions. They settle very fast because of their density of 6.14 g/cm³. The use of basic lead carbonate is also limited by its low chemical stability and toxicity of its byproducts as well as toxicological concerns in its application areas. Today less than 1000 t of basic lead carbonate pigments are produced annually worldwide.

3. Bismuth Oxychloride

Bismuth oxychloride is produced by hydrolysis of very acidic (pH < 1.0) bismuth solutions in the presence of chloride. The crystal quality can be varied by careful adjustment of bismuth concentration, temperature, pH, pressure, reactor geometry, and addition of surfactants. The usually tetragonal bipyramidal structure can be flattened to platelets with a high aspect ratio. Products with an aspect ratio of 10–15 show low luster and a very good skin feel and are used as fillers in cosmetics.³⁹ Crystals with higher aspect ratios show an exceptional luster and are mainly used for nail polish.

The low light stability, the fast settling caused by the high density of 7.73 g/cm³, and the lack of mechanical stability limit the use of BiOCl in technical applications. Therefore, it is mainly used in cosmetics, but also in buttons and jewelry. The light stability can be improved to some extent by cerium doping⁴⁰ and UV absorbers. The current world market is about 400 tons per year.

4. Micaceous Iron Oxide

Micaceous iron oxide consists of pure or doped hematite ($\alpha\text{-Fe}_2\text{O}_3$). In nature it is found already in the form of platelets,⁴¹ for example, in large quantities in Kärnten, Austria. Its density is 4.6–4.8 g/cm³; its natural color is dark gray with low luster. Natural micaceous iron oxide is nearly exclusively used in corrosion protection coatings.

Micaceous iron oxide can also be obtained by hydrothermal synthesis in alkaline media. However, the dull dark color is as unappealing as that of the natural product. If substantial amounts of dopants are incorporated,⁴² the aspect ratio can be increased up to 100, resulting in a much increased luster. The color can be also shifted to a more attractive reddish brown so that the products can be used for decorative purposes.

The most important dopants are Al_2O_3 , SiO_2 , and Mn_2O_3 . They can enforce a spinel structure. SiO_2 yields thin small platelets, Al_2O_3 yields thin larger platelets, and Mn_2O_3 reduces the thickness.⁴³ The addition of ZrO_2 , B_2O_3 , P_2O_5 , SiO_2 , or additional Al_2O_3 reduces the agglomeration in application. Chromates, molybdates, wolframates, permanganates, and titanates can be used to create different color shades.

The starting material $\text{Fe}(\text{OH})_3$ or better FeOOH is heated in an alkaline suspension together with the dopants to temperatures above 170°C , typically 250 – 300°C . Ferrates are probably formed as intermediates.⁴³ After several minutes to hours, platelets of doped iron oxide are obtained. In a second reaction phase, the pH is further increased so that platelets grow and form flat basal faces.

5. Titanium Dioxide Flakes

Titanium dioxide flakes are produced by breaking down a continuous film of TiO_2 . The most efficient process is therefore is a web-coating process involving a thermal hydrolysis of TiOCl_2 on the web.^{44,45} Alternative procedures are the application of titanium alkoxide on a smooth flat surface and cracking the resulting film into flakes by steam treatment,⁴⁶ the application of a TiO_2 sol on a glass surface and scratching off the resulting film,⁴⁷ the application of TiOCl_2 solution onto a gelatin film and dissolving the gelatin film, vacuum deposition,⁴⁸ the treatment of potassium titanate fibers with acid and subsequently with heat,⁴⁹ or creating and breaking hollow TiO_2 particles from a surfactant– TiO_2 sol mixture.⁵⁰ Using the latter process, often concave shell-type flakes are obtained.

Substrate-free TiO_2 flakes can also be derived from TiO_2 –mica pigments⁵¹ or flaky TiO_2 – SiO_2 pigments⁵² by dissolving the substrate in strong acids and/or strong alkalies.

The titanium dioxide flakes produced by the methods mentioned above are not single crystals but quite porous and, lacking the mechanical support of a substrate, hence brittle. Therefore, they are not used in technical applications in which mechanical stress is exerted. Commercial products are available for the cosmetic market.

The TiO_2 flakes can be reduced to titanium suboxides yielding a dark bluish mass tone in addition to the interference color.⁵³

6. Flaky Organic Pigments

Some organic pigments can be forced to crystallize in flake form, such as 1,4-diketo-3,6-diarylpyrrolo-(3,4-c)-pyrrole (DPP),^{54,55} 2,9-dichlorochinacridone,⁵⁶ and metal phthalocyanines.⁵⁷ However, the difference between their refractive index and that of typical

applications such as lacquer is too small to generate strong interference colors. In most cases, the aspect ratio of these crystals is also much smaller than that of the inorganic pigments mentioned above.

B. Pigments Formed by Coating of Substrates in the Gas Phase

Compared to liquid-phase coatings, gas-phase reactions have the advantage of higher reaction temperatures and a higher tendency for epitaxial growth. Solvents and electrolytes also do not appear as side products that might contaminate the optical layers. Gas-phase reactions allow smooth metal coatings, even as multiple coatings. However, gas-phase processes are, in general, more difficult to handle. One problem is corrosion, for example, by TiCl_4 , or toxicity of the precursors, for example, of $\text{Fe}(\text{CO})_5$. It is also more demanding to fluidize the substrates in the gas phase than it is to disperse them in water.

1. Coatings onto Metal Flakes

Oxide-coated metal flakes can be prepared by atmospheric oxidation at elevated temperatures. Colorful products can be obtained when the surface of titanium flakes is oxidized to titanium suboxides.⁵⁸ Iron or iron alloy flakes can be also oxidized.⁵⁹ With this technique the resulting surfaces are rather rough, especially for thicker oxide coatings. Only the corresponding oxide can be derived from the metal flake.

It is quite difficult to handle metal flakes in the liquid and especially the aqueous phase because of agglomeration and corrosion. Therefore, gas-phase coating procedures have been developed.

Aluminum flakes can be coated with iron oxide in a CVD process.⁶⁰ These are commercially the most important pigments based on CVD. The metal flakes are fluidized in nitrogen gas at temperatures around 450°C . Then the reagents, $\text{Fe}(\text{CO})_5$ and O_2 , are injected into the fluidized bed. For a proper coating they must be highly diluted in an inert gas. Sometimes water vapor is added to reduce electrostatic charging. The thickness of the coating is controlled by the reaction time. The only side product is carbon monoxide, which is catalytically oxidized to CO_2 .

It is not known yet whether the reagents form an Fe_2O_3 aerosol which then coats the aluminum flakes or whether they react at the hot flake surface.⁴³ However, the epitaxial growth, the low porosity, and the absence of cracks in the coating support the latter mechanism. The problems with this coating process are to avoid the formation of stack-like agglomerates during the coating process, to fluidize the rather small particles, and to handle the reactive reagents at elevated temperatures.

The aluminum flakes can be coated with aluminum oxide and/or silicon dioxide in the liquid phase before the CVD process⁶¹ to reduce the reactivity of the metal and to create multilayer color effects.

Metal halogenides are difficult to use as gas-phase precursors for the metal oxide coating because of the reactivity of the metal flakes and the corrosion of steel in chloride atmospheres. The use of TiCl_4 and water vapor was described⁶² about 10 years ago.

However, no commercial products have been introduced as yet.

2. Coating onto Nonmetallic Flakes

Mica flakes can be coated in CVD processes using the same techniques as those discussed for metal flakes. In addition, one can also use metal chlorides as precursors for the oxide coating on mica.⁶² However, essentially the same products can be obtained more easily by precipitating the oxides from the liquid phase. Commercially available are iron oxide/mica pigments for which $\text{Fe}(\text{CO})_5$ is used as the precursor in a process very similar to the one for Al flakes.

At higher temperatures, golden coatings of TiN on mica can be obtained from TiCl_4 and NH_3 .⁶³ Glass flakes can be coated with Si, which is then oxidized to dark SiO_2 .⁶⁴ Commercial products that are based on the latter processes are not available yet.

C. Pigments Formed by Coating of Substrates in the Liquid Phase

1. Metal-Oxide-Coated Mica

Today the commercially most important pearlescent pigments are metal-oxide-coated mica particles, see Figure 8. Their synthesis was first published in 1942.⁶⁵ However, a commercial use came only after the base patent of Du Pont⁶⁶ in the early 1960s and further improvements by Mearl⁶⁷ and Merck.⁶⁸ The coating of most products is formed with TiO_2 , hematite ($\alpha\text{-Fe}_2\text{O}_3$), or mixed oxides thereof. But other oxides and inorganic colorants are used to form layers on mica as well: green Cr_2O_3 ,⁵¹ black Fe_3O_4 ,⁶⁹ ferric ferrocyanide (iron blue),⁷⁰ cobalt blue, silver white bismuth oxychloride,⁷¹ SnO_2 ,⁷² and ZrO_2 .⁶⁶

Coatings of black SiO_2 ,⁷³ deeply colored oxide bronzes (wolframates, molybdates),⁷⁴ yellow bismuth vanadate,⁷⁵ and metal sulfides⁷⁶ have also been reported; however, there are no commercially available products yet.

The mica substrate acts as a template for the synthesis and as a mechanical support of the thin optical layer. For nearly all commercial products, muscovite mica is used because the raw material is easily available and can be cleaved to thin platelets of high aspect ratio. However, natural mica contains small amounts of iron (1–2% Fe_2O_3) which cause the slightly yellow mass tone seen in high pigment concentrations. Therefore, a few products have been developed that are based on synthetic fluorophlogopite,⁷⁷ which does not have iron impurities but is more expensive than natural muscovite. On the other hand, there are also some products based on natural phlogopite, which is darker than muscovite.

Recently, multilayer oxide coatings have been developed based on a mica substrate. These products have an alternate order of high-refractive and low-refractive oxides precipitated onto mica. The low-refractive oxide layer consists of SiO_2 and/or Al_2O_3 . Its thickness is normally adjusted in a way that the layer becomes optically active.⁷⁸ Figure 9 shows the stronger reflectivity of such a multilayer pigment that consists of mica coated with 160 nm of anatase-

TiO_2 , 85 nm of SiO_2 , and 160 nm of anatase- TiO_2 compared to the conventional green interference mica pigment with one layer of 160 nm of anatase- TiO_2 . When a thin not optically active layer is precipitated, the grain growth of the main oxide layer is started again and a coloristical improvement is observed.⁷⁹

Today TiO_2 -coated mica is obtained using the following chloride process: TiOCl_2 solution is slowly added to a mica platelet suspension at a pH value of about 2 and temperatures of 60–90 °C. The reactor geometry and mixing conditions have to be carefully controlled. Using this titration process, the oxide layer thickness can be well adjusted to yield defined interference colors, as seen in Figures 8 and 9. An alternative process uses titanium oxysulfate: A suspension of mica platelets in a TiOSO_4 solution is heated to undergo a thermal hydrolysis.⁶⁶ This process does not allow a precise adjustment of the layer thickness and also shows no significant economic advantages over the chloride procedure. It is, therefore, only used for the generation of thinner silver-white TiO_2 layers, whereas the titanium oxysulfate as a raw material is more available than the chloride.

When TiO_2 is precipitated onto muscovite under reaction conditions unfavorable for side precipitation, e.g., pH > 1.5, only the anatase modification is formed. Even after annealing at 1000 °C, no rutilization is found in the layer, whereas the free titania turns completely into rutile at about 700 °C.⁸⁰ When the less usual substrate phlogopite is used instead of muscovite, a partial conversion to rutile is observed above 850 °C. Eskelinen sees the reason for this difference in a migration of Al ions from the mica into the anatase layer, which then inhibits the phase transition.^{81–85} But the anatase modification is also solely found below 1000 °C, if aluminum-free SiO_2 or alumina itself is used as a substrate instead of mica. The most probable explanation is a considerable constraint in the film which counteracts the volume contraction during rutilization and delays the phase transition.^{80,86}

The anatase layers on mica show a preferred crystal orientation when they are very thin,^{81,86} e.g., < 40 nm. The upper layers then lose the preference. It is also known that uncalcined layers show a deviation from the lattice parameters of bulk anatase, which diminishes after calcination.⁸⁶ Both observations support a template effect of the muscovite substrate.

Rutile has a higher refractive index and, therefore, yields a stronger pearlescence than anatase,⁸⁷ see section II and Table 1. Therefore, processes have been developed to create a rutile layer onto mica: A thin layer (about 1 wt %) of SnO_2 is precipitated as a continuous layer onto the substrate, and then the TiO_2 layer is created using the usual process. SnCl_2 ⁸⁸ or better SnCl_4 ⁸⁹ can be used as precursors for the SnO_2 precoating. SnO_2 acts as a template because its lattice parameters $a = 4.737$ and $c = 3.186$ are close to those of rutile, $a = 4.593$ and $c = 2.958$.⁹⁰ Instead of the colorless SnO_2 (which is restricted for the use in cosmetics in Japan), Fe_2O_3 can be used to create rutile-mica pigments.⁹¹ However, the necessary amount of iron oxide creates a yellowish mass tone

of the resulting pigment. The rutile layers on mica show a little larger preference in the crystal orientation than anatase.⁸⁶

The desired interference color determines the thickness of the titania layer. This relation can be calculated using the equations mentioned above.⁵ For a silver white pigment 50 nm of anatase is needed and for a blue interference color about 120 nm. However, these published values are calculated under the assumption of dense layers and are not taking the porosity for which a correction could be applied using eq 18 into account.

The titania in these layers can be reduced to dark-colored titanium suboxides using NH_3 ,⁹² carbon, metals, or metal hydrides⁹³ as reducing agents. The titanium suboxides are usually accompanied by oxynitrides when NH_3 is used.⁹²

The titania layers can be doped with carbon black⁹⁴ or organic dyes. They can also be coated with thin layers⁹⁵ or dots of metals to create a darker mass tone (with silver,⁹⁶ nickel,⁹⁷ or mixtures of various metals⁹⁸).

Hematite coatings on mica are usually generated from two different precursors. Solid iron (II) sulfate can be added to a suspension of mica platelets at temperatures above 60 °C. A better control of the coating layer quality is found when FeCl_3 solution is slowly titrated to a mica suspension^{86,99} in a way very similar to the titanium oxychloride titration mentioned above. The mica platelets can be optionally precoated with a thin layer of titania.

The resulting dried iron oxide layer consists of hematite ($\alpha\text{-Fe}_2\text{O}_3$) and sometimes minor amounts of goethite ($\text{FeO}(\text{OH})$). It is formed as nanocrystallites of 20–40 nm diameter which show a strongly preference of crystal orientation due to a template effect of the muscovite.⁸⁶ During annealing at temperatures of 700–900 °C, the grainy layer structure sinters to a less porous glasslike crystalline plate.⁸⁶ Doping with a borate or phosphate can prevent this sintering. The layer thickness is about 75 nm for a bronze and 85 nm for a red color. As mentioned in section II.D, the interference color as well as the mass tone of these light-absorbing layers are a function of the layer thickness.

Layers of golden Fe_2TiO_5 (pseudobrookite)¹⁰⁰ are formed if stoichiometric amounts of Fe_2O_3 and TiO_2 are precipitated one after another onto mica and then calcined above 800 °C. A coprecipitation reduces the temperature for the conversion to pseudobrookite to some extent. If a mixed iron oxide/titania layer is calcined under a reducing atmosphere, silver gray FeTiO_3 (ilmenite)¹⁰¹ is obtained.

2. Coatings onto SiO_2 Flakes

Instead of mica, SiO_2 flakes can be used as a substrate for pearlescent pigments.¹⁰² The SiO_2 flakes are produced by a web-coating process.⁴⁵ Synthetic SiO_2 flakes offer three advantages over the use of natural mica: (1) the thickness of the SiO_2 substrate can be controlled in the preparation so that at the end a pigment with a true optical three-layer system is obtained; the interference color of those systems is stronger than for the conventional mica pigments

for which the effect of the mica is "wiped out" by a broad thickness distribution; (2) as synthetic substrates they do not have the small iron impurities that cause slightly yellow mass tone of natural mica; (3) SiO_2 has a lower refractive index (1.46) than mica (about 1.58) and, therefore, leads to a stronger interference effect.

SiO_2 flakes have higher production costs than for mica due to the large area and high rotation speeds needed in the web coating. Silver white pigment are only accessible by mixing batches with different substrate thicknesses. The reason lies in the optical three-layer system that is found when all substrate particles have the same thickness.¹ As a coating, the same oxides and colorants can be used as for mica substrates. Commercially available glass flakes can be coated with metal oxides as well.¹⁰³ However, these flakes are generally too thick for an optical three-layer system with a strong reflection.

Multilayer oxide coatings have been created on the base of SiO_2 substrates.⁷⁸ They show even stronger and clearer interference colors than the mica-based multilayer pigments due to the fact that the substrate becomes part of the optical system. At the present time, pigments based on SiO_2 flakes are at the beginning of their commercialization.

3. Coatings onto Al_2O_3 Flakes

Thin Al_2O_3 flakes can be obtained by applying an alumina sol on a smooth surface and scratching off the resulting film.⁴⁷ However, this process can hardly be used for an industrial production. Thin hexagonal monocrystalline Al_2O_3 flakes can also be produced by hydrothermal processes. The thickness of the resulting flakes is not uniform. Therefore, the resulting coated pigments merely assume a dull pearlescence.

Al_2O_3 flakes of a higher quality are produced by the following steps:¹⁰⁴ An aqueous solution of an aluminum salt is mixed with small quantities of a titanium salt and phosphate. After neutralization, a sol or suspension is obtained, which is then dried and heated to 900–1400 °C. After washing, very thin flakes are found which consist of corundum and show a high aspect ratio, a very narrow thickness distribution, and very smooth surfaces. The thickness can be controlled by the doping and reaction conditions. The resulting flakes are used as substrates in the aqueous-phase processes described above to prepare pearlescent pigments of very high luster. The advantage over the mica substrate lies mainly in the fact that all Al_2O_3 flakes have about the same thickness, which leads to true optical three-layer systems as for the SiO_2 flakes.

4. Coatings onto Other Flaky Substrates

Flaky barium sulfate can be used as a substrate in the preparation of UV-absorbing pearlescent pigments.¹⁰⁵ It can be coated with UV-absorbing zinc oxide and optional TiO_2 and cerium oxide components. The main use of these materials is in cosmetics. Titanium dioxide flakes can be used as pigments themselves, see above, but can also be coated with metal oxides¹⁰⁶ or multiple layers of oxides.¹⁰⁷ Because of their tendency for hydrolysis and corrosion, it is

difficult to coat metal flakes in the liquid phase. All reasonable attempts were made using organometallic compounds in nonaqueous or wet organic solvents. For example, titanium flakes can be coated with TiO_2 using the well-established sol-gel process based on $\text{Ti}(\text{OEt})_4$.¹⁰⁸ Aluminum flakes have been coated with a ZrO_2 layer that was doped with cobalt and iron to create a mass tone.¹⁰⁹ The surface of aluminum flakes can be oxidized in aqueous media, and the resulting aluminum oxide layer is used as an absorbent for organic and inorganic colorants.¹¹⁰

V. Pigments and Films Based on Dichroism

Interference and angle-dependent color effects can also be achieved by layers or particles based on liquid crystal polymers (LCP).¹¹¹ Such effects can, for example, be produced by small plate-like substances which consist of a LCP material itself or by small platelets which are uniformly coated with a cross-linked liquid crystalline polymer in a chiral-nematic arrangement.¹¹²

Liquid crystals are organic compounds in a state of matter intermediate between that of an isotropic liquid and an anisotropic crystalline solid.¹¹³ Most liquid crystalline molecules are markedly elongated and rod like. In nematic liquid crystalline materials, the direction of the long molecular axes (director) is arranged parallel to each other. Adding a chiral molecule to a nematic phase causes a superstructure comparable to the steps of a spiral staircase. The structure can be understood as being composed of nematic layers having the director rotated by a certain angle with respect to an adjacent layer, eventually building up a helical array (Figure 10).

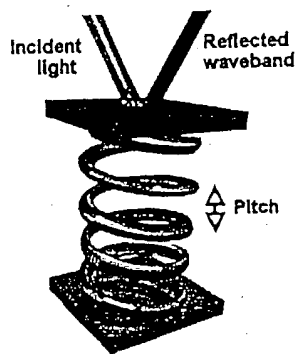


Figure 10. Scheme of a liquid crystal film.

The thickness of a 360° turn of the director represents the pitch length p of the helix.¹¹¹ The color design of LCP pigments in paint films or of pure LCP films has its origin in an interference phenomenon.^{111,112} In this case, only incident light with a wavelength equal to the LCP lattice separation interferes and is reflected.

Due to the change of refractive index from layer to layer, the helical structure gives rise to interference effects (Figure 11). When white light is incident normally on a film or an oriented arrangement of platelet-like particles of a cholesteric material with the helical axis perpendicular to the substrate, selective reflection of a finite wavelength band occurs similar to Bragg X-ray reflection. The reflected band

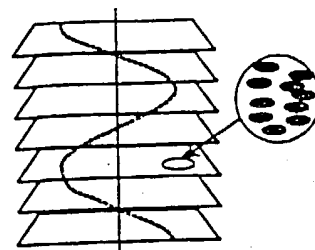


Figure 11. Chiral cholesteric (nematic) liquid crystal structure. The dotted line shows a helical path within the medium. Pitch length $p = 360^\circ$ rotation.

is centered about a wavelength λ_0 , which is related to the helical pitch length p of the phase and its average refractive index n by $\lambda_0 = np$.^{111,112}

On the other hand, a structure which has a helical superstructure with no change in the refractive index can also reflect light just like cholesteric phases.¹¹⁴ In this case, it is not so much a change in the refractive index that gives rise to the optical effect but rather the superstructure.

The reflected light is circularly polarized with the same sense of polarization as the helical sense of the liquid crystal phase. Light circularly polarized in the opposite manner is transmitted through the sample together with those wavelengths of light not being reflected. Light experiences a double refraction as a result of the anisotropy of the system. The bandwidth $\Delta\lambda$ of the selectively reflected band is described by the relation $\Delta\lambda = p\Delta n$. The angular dependence for an incident and observed angle Θ is given by $\lambda_\Theta = \lambda_0 \cos \Theta$.

The reflected light waves from the layers increase the intensity of the total reflection. The maximum reflectivity of one polarization state requires at least 6 helices or a thickness of about $3 \mu\text{m}$.¹¹¹ The most efficient reflection is given by layers with a thickness of up to $10 \mu\text{m}$.

Cholesteric materials are temperature sensitive and show a thermochromic effect. The reason for this is that the pitch length of the helix and the refractive index are temperature dependent.^{111,112,115}

Liquid crystal polymer films are transparent to visible light, including in the form of platelets and coatings on substrates dispersed in a transparent paint film. These films need to be deposited on a dark substrate or in an effect lacquer with a dark base coating. Light is transmitted through the liquid crystal polymer, but some wavelengths are absorbed by the dark substrate or base coating. The liquid crystal polymer will be aligned parallel to the substrate, either as a film coating or on the interference pigment platelets within the paint film. This will then show a particular color in the orthogonal view and another color when observed at an angle. Such angle-dependent color phenomena give a very striking effect, which is of great interest for security applications. Paint coatings incorporating such pigments must be constructed of several layers with the liquid crystal materials in one of the inner layers only.

A number of this type of interference pigments are based on polysiloxanes. They are formed first as a thin cross-linked film of liquid crystalline polymers

which are then ground to small platelets. The interference pigments themselves are colorless and transparent. The color effect is based on the regular structure and on the uniform arrangement of the liquid crystalline molecules. This gives rise to the reflection and subsequently interference with light of a particular wavelength. The other parts of the light go through the pigment particles. Very interesting color effects are possible based on these optical principles.

Liquid crystal polymers are side chain polymers which are usually prepared in a procedure, employing the coupling of a H-siloxane main chain with ω -alkenyl bearing mesogenic groups via catalytic hydrosilylation.¹¹⁶ There is an extension of this concept to different geometric and chemical classes of backbone siloxanes, i.e., linear,¹¹⁷ cyclic,^{118,119} and cage-like siloxanes.¹²⁰ Siloxanes with a great variety of substituents are used.¹²¹

For use as optical films or individual pigment particles, liquid crystalline materials are required which are stable within a suitable temperature range. Thermotropic materials can, therefore, not be used for this purpose. The problem of obtaining mesomorphic structures over a broad temperature range can be overcome in two special ways. First, it is possible to fix the structure in the glassy state, thus requiring a high T_g , or second by cross-linking. Chemical cross-linking is generally done photochemically; this leads to a fast polymerization. Contrary to thermal cross-linking, a wide choice of cross-linking temperatures is possible.

Liquid crystalline siloxanes are limited with respect to the glass transition in comparison to other backbone systems, such as poly(meth)acrylates. Glass transition temperatures of up to 80 °C can be achieved,¹²¹ but there is a limit for the variations of the mesogenic groups. Therefore, cross-linking is the preferred method. The presence of at least some polymerizable moieties within the side chain groups is necessary. Typical examples for these groups are epoxides, cinnamates, or methacrylates.

To obtain cholesteric films with good optical properties, the cross-linkable siloxanes must have a low viscosity. Small molecules containing 3–10 siloxane units are preferred. Cyclic siloxanes as well as linear siloxanes can be used.

There are two ways to introduce the cross-linking moiety to a siloxane backbone.¹¹⁶ One possibility is to couple an OH-protected unit to the siloxane chain followed by methacrylation of the deprotected OH groups.¹²² Another way is to directly couple the methacrylate-bearing unit to the siloxane backbone chain.¹²³ The second way should be feasible at least for small and medium-sized siloxanes, as the reactivities of ω -alkenes and methacrylates toward hydrosilylation differ by a factor of at least 10, thus minimizing premature cross-links via hydrosilylation.

The reflection wavelength of liquid crystalline layers or particles can be tuned in the region from 390 to 670 nm by mixing suitable cholesteric liquid crystal compounds. The wavelength of reflection I_T is inversely proportional to the concentration of chiral component, yielding the following equation¹¹⁶

$$\frac{I}{I_T} = \text{const} \cdot C_{\text{Chiral}} \quad (19)$$

C_{Chiral} is the concentration of the chiral component in the mixture. In some cases, more than one chiral component is used, e.g., C_1 and C_2 . Therefore, the relation

$$C_{\text{Chiral}} = xC_1 + (1-x)C_2 \quad (20)$$

is used, where x is the fraction of C_1 in the mixture. Combining eqs 19 and 20 leads to the relation between the wavelength of reflection and the fraction C_1 in the mixture¹¹⁶

$$I_T = \frac{1}{ax + b} \quad (21)$$

The coefficients a and b must be determined and then compared with the experimental data. I_T is dependent on the curing temperature. When cross-linkable cholesteric liquid crystalline siloxanes are cured, two things happen to the helical pitch: It reduces the helical pitch by about 2% due to shrinkage of the material during the curing process, and it becomes fixed to this value. Depending upon the temperature of curing, the reflection wavelength can vary, for example in the red, green, or blue region.

After curing, the I_T becomes virtually independent of temperature up to 140 °C. A very small residual increase (less than 0.2 nm/K) can be attributed to the thermal expansion of the cured polymer.

Several applications were developed to take advantage of the specific properties of the cross-linkable cholesteric liquid crystalline siloxanes. For example, optical filters can be made of cross-linkable and noncrosslinkable liquid crystalline siloxanes.^{124,125} Another application is the use of glassy cholesteric materials as meltable paints.¹¹¹

Liquid crystalline polysiloxanes are also suitable for optical write-once storage.¹²⁶ A high contrast in reflectivity for data storage is obtained with these materials at wavelength and energies which can be supplied by commercially available semiconductor lasers.

On the other hand, small, insoluble platelets can be used as iridescent pigments.^{127,128} Such platelets can be suspended in inorganic and organic media, especially lacquers. The spray technique is mostly used for the application in paint films. The color effects are very strong if black substrates are used to ensure the absorption of the transmitted light. Very interesting colors can be obtained when combined with other effect pigments or in mixtures with conventional pigments.¹²⁹

Interference pigments based on liquid crystalline materials are prepared by a doctor-blade coating of the polymers in the liquid or liquid crystalline state on an even surface. The doctor-blade process leads to a thin film wherein a homogeneous orientation of the molecules takes place. It is only after this orientation process that the film shows an interference color. The films are then cured and crushed by

special techniques to yield platelets of liquid crystalline polymers showing interference effects.

VI. Pigments and Films Based on Holography and Gratings

Holography, as a field of optical science in which wave fronts are recorded, stored, and recovered, can be described as the technique of using diffraction to transform one wave front into a second in a prescribed manner.¹³⁰ A hologram is generally a two-dimensional mask which contains structures with details on the order of the wavelength of the transformed wave front. The technique of holography may be applied in the entire spectrum of electromagnetic waves (visible, infrared, ultraviolet, X-ray) and non-electromagnetic waves (acoustic waves, matter waves such as electrons).

Mass replication of holograms is commonly accomplished through the embossing of clear or reflective films.^{130,131} During a typical embossing process, a master hologram is recorded in a photoresist which, upon development, exhibits a surface relief mapped from the intensity distribution of the holographic interference pattern. The photoresist master is then copied onto a metal stamping master. The stamping master is then heated and pressed in contact with a thermoplastic material, which is then separated from the stamping master and contains a replication of the original hologram structure. Injection molding is used as an alternative. Thousands of impressions may be produced from one stamping master, and the resultant embossed plastic holograms may be reconstructed in transmission or reflection. In the latter case, the plastic is usually coated with aluminum to enhance diffraction efficiency.¹³⁰

Holograms can perform the functions of basic optical elements, e.g., holographic diffraction gratings, holographic multilayer mirrors, diffractive lenses, chirped holograms as scanners, etc.^{130,132} Diffraction patterns and embossments, and the related field of holograms, have begun to find wide-ranging practical applications due to their aesthetic and utilitarian visual effects. In recent times, the diffraction grating technology has been employed in the formation of two-dimensional holographic images which create the illusion of a three-dimensional image to an observer. This holographic image technology can be used for the manufacture of very attractive displays. The concept of using holographic images to discourage counterfeiting has meanwhile found wide application.

The holographic exposure may consist of the interference pattern produced between two plane waves, where the period Λ along the surface of the grating is controlled by the exposing wavelength λ and the angles, θ_1 and θ_2 , which plane waves subtend with respect to the surface normal.¹³⁰ These parameters are connected by the equation

$$\Lambda = \frac{\lambda}{\sin \theta_1 - \sin \theta_2} \quad (22)$$

At the beginning, diffraction gratings were formed by scribing closely and uniformly spaced lines on polished metal surfaces using special "ruling en-

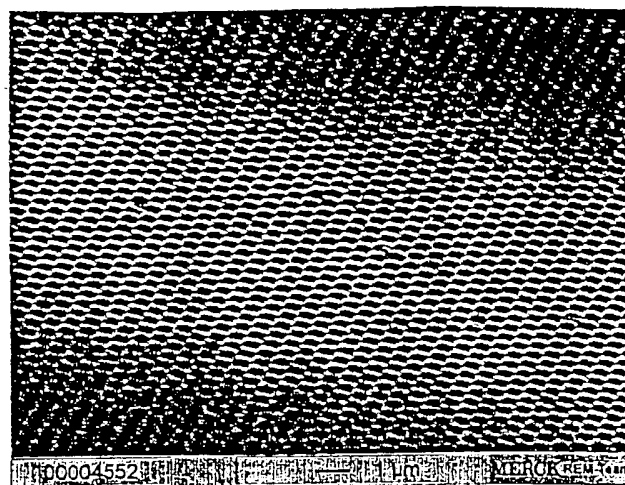


Figure 12. SEM picture of a holographic film made by aluminum metal deposition on a polymer film to be used for the production of holographic pigments. The average distance between the peaks of the structures is about 800 nm.

gines".¹³³ Subsequently, techniques were developed to reproduce a master diffraction grating by shaping a moldable material against the master diffraction grating surface. The development has led to a technology where thermoplastic films are embossed by heat softening the surface of the film and then passing them through embossing rollers which impart the diffraction grating or holographic image onto the softened surface. Sheets of effectively unlimited length can so be decorated with the diffraction grating or holographic image on a surface. The decorated surface of polymers is sometimes sufficiently reflective that there is an optical effect from the diffraction grating already without further processing, because the incident light is reflected by the facets of the decorated surface.¹³³ The full optical effects, however, require metallizing of the embossed polymer surface.

Diffraction gratings manufactured in this manner are free from so-called "ghosts" caused by systematic ruling errors. They can be produced rapidly with a large aperture. Further, holographic diffraction patterns and embossments can be recorded throughout a volume recording material rather than as a surface modulation. Such volume holograms can be recorded as transmission or multilayer reflection gratings.¹³⁰ In the former case, they can exhibit peak diffraction efficiencies near unity and spectral bandwidths of 400 nm.¹³⁴ Holographic multilayers can be applied as notch filters with bandwidths on the order of 10 nm and efficiencies of 99.99%.

Grinding of holographic films, when done in a suitable manner, can lead to small holographic particles. These so-called holographic or hologram pigments are relatively new materials for attaining special optical effects in different application media.^{133,135,136} A structure of a holographic pigment particle is shown in Figure 12. Generally, any hologram base material on which an interference band corresponding to the wave face of light from a substance is formed as a hologram image may satisfactorily be used with no specific limitation for

the production of holographic flake pigments.¹³⁵ For practical use, holographic mirrors are preferred for the manufacture of those pigments. A holographic mirror is the simplest reflection hologram. It can be created by splitting a laser beam and recombining the beams at a photosensitive layer on the thermoplastic film (two-beam method).¹³⁶ Alternatively, it can be created by projecting a laser beam through the photosensitive layer onto a mirror (single-beam method).

Holographic flake pigments frequently have a band-center wavelength of about 380–1100 nm and an effective bandwidth of about 10–200 nm.¹³⁶ The pigment particles have a thickness of about 1–100 μm , an average diameter of about 10–300 μm , and a thickness-to-diameter ratio from about 1:2 to about 1:60.¹³⁶ Holograms can be converted to pigment particles of the desired size by any conventional means, such as grinding, ball milling, attritor grinding, or two-roll milling. One possibility that can be used is to cool the hologram below its glass transition temperature, for example in liquid nitrogen, before grinding. It is also possible to grind the hologram in cold water, such as ice water. As an alternative, the grinding equipment can be refrigerated to cool the hologram to below its glass transition temperature.

Holographic flake pigments are useful for the preparation of decorative coatings that can be used to emphasize the lines and contours of a three-dimensional surface. They can also be used for the preparation of exterior finishes for automobiles. Another possibility is the application in molded plastics to provide a decorative appearance, e.g., in tiles.

VII. Pigments Formed by Grinding a Film

Optical coatings that shift color with viewing angle have been adapted into optically variable films, pigments, and inks during the last years. These coatings are based frequently on metal-dielectric multilayer thin structures having large color shifts with angle, high chroma, a large color gamut, and light fastness.

Different colors are produced by precisely controlling the thickness of the multilayers in the coating's structure. To maintain tight color tolerance, the layer thickness must be controlled to within a few atoms. The schematic of the light interference multilayer structure is shown in Figure 3.

The metal layers frequently consist of chromium (semitransparent absorber metal) or aluminum (opaque reflector metal). Silicon dioxide or magnesium fluoride are the materials mostly used for the dielectric layers. In the case of pigment particles, there is a symmetrical arrangement of the layers, as shown in Figure 13, whereas optical coatings can also consist of a system of unsymmetrical layers. All these arrangements are the basis for an optical phenomenon called the Fabry–Perot effect.

Such multilayer interference configurations filter the spectrum into a sequence of high-reflectance regions surrounded by low-reflectance regions and thus lend themselves, in principle, to high-purity color production. The detailed spectral characteristics

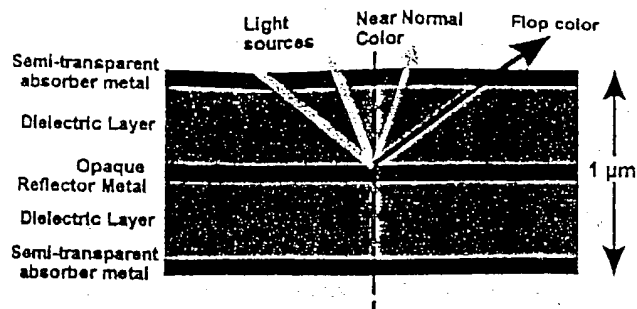


Figure 13. Scheme of the design of optically variable pigments (OVP).

can be widely controlled by controlling the specific design parameters. The metal-dielectric multilayer systems consist of a structure which can be written in the form $(M_1 - \alpha D)^q - M_2$, where M_1 and M_2 are the metal components (generally different), D represents a dielectric layer, α is the unit of quarterwave optical thickness of the dielectric layer, and q is the number of periods in the stack.¹³⁷ There are many variations which are obtainable within this framework by varying parameters, such as refractive index, thickness ratios, number of periods, etc. Additionally, a number of variations and extensions of the designs can be obtained by using multicomponent periods, altering the period makeup to consider symmetrical periods, etc.

The metal-dielectric stack, in its simplest form of a three-layer combination can be regarded as a Fabry–Perot reflection-type interference filter.¹³⁷ Such a design will be of the form $M_1 - \alpha D - M_2$, where M_2 is a highly reflecting, essentially opaque metal layer and M_1 is a rather thin metal film with high absorption properties. A sequence of high- and low-reflectance wavelength regions can be realized corresponding closely to the conditions that give rise to the nodes and antinodes of the standing wave electric field established by the reflector M_2 . In the vicinity of an antinode wavelength position, where the electric field intensity is a maximum, induced absorption can be shown to occur in the thin metal layer M_1 resulting in a low reflectance. At a node position, M_1 has little effect on the reflectance of M_2 and the overall reflectance remains high. The separations between the node and the antinode wavelength locations and thus between the low- and high-reflecting regions correspond to quarterwave optical thickness changes in the dielectric layer D . The basic reflectance profile for the three-layer metal-dielectric design as described here will be essentially retained in design employing additional periods of $(M_1 - \alpha D)$.¹³⁷

For obtaining optimum performance in optically variable articles using a metal-dielectric design, one would take for M_2 the highest reflecting metal consistent with overall good durability properties, for D the lowest usable refractive index material, and for M_1 a metal with high absorption properties. High potential absorption properties occur for metals with a high product $n \cdot k$ (n refractive index, k absorption coefficient). For example, instead of using chromium for the semitransparent absorber metal layers M_1 , materials such as nickel and Inconel could also be

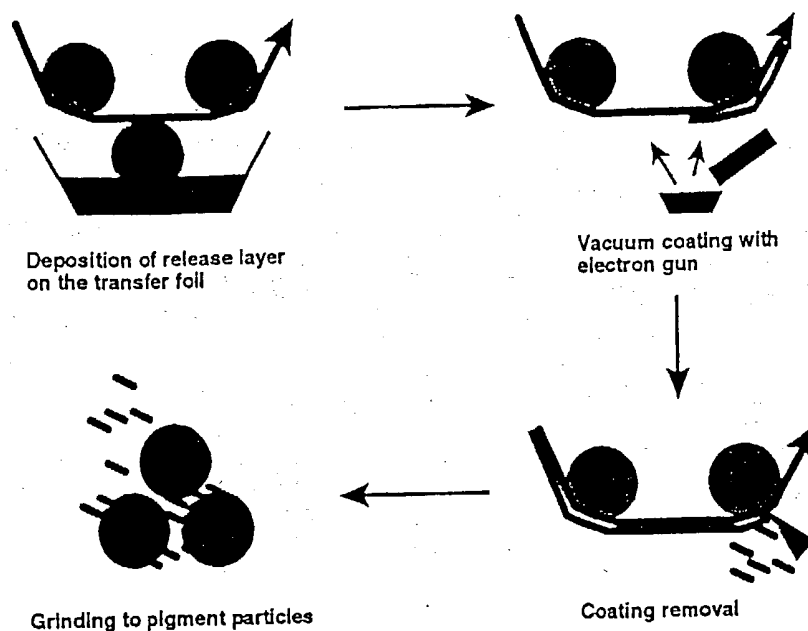


Figure 14. Scheme of the production of optically variable pigments (OVP).

utilized. Instead of silicon dioxide or magnesium fluoride for the dielectric layers *D*, materials such as aluminum oxide or indium oxide could also be used. Finally, instead of aluminum as the opaque reflector metal, layer materials such as gold, copper, and silver could be used for this purpose.¹³⁸

In the foregoing discussions, it has been already described that for flaky pigment particles, a symmetrical arrangement of the layers is necessary. A minimum of five layers and for some optical purposes more may be required. The need for many layers tends to make such a design relatively impractical in any high-volume coating production. Therefore, for practical use, only the five-layer arrangement plays a role.

The pigment flakes can typically be manufactured sequentially in a series of specialized roll-coating machines.¹³⁹ In the first machine a carrier film, the so-called release layer, is deposited on a moving polymer web (transfer foil). This release layer is soluble in organic solvents to remove the later formed multilayer film from the web at the end of the process. After depositing this release layer, the transfer foil is placed in a vacuum deposition roll coater and the first metal layer (e.g., chromium) as the semitransparent absorber metal is deposited followed by the first dielectric layer (e.g., magnesium fluoride) and the opaque metal layer (e.g., chromium). The second dielectric layer and the second semitransparent absorber metal layer follow by the same deposition process. After this symmetrical multilayer interference coating has been deposited, the coated foil is removed from the vacuum chamber. In a next step, the formed thin multilayer film is removed from the supporting transfer foil by dissolving the release layer. The transformation into pigment particles is done by grinding the removed part of the film into small platelets which show now pigment dimensions (thickness of 0.2–2 μm , diameter 1–100 μm). The whole process is shown schematically in Figure 14.

Besides the here described metal-dielectric multilayer pigments, there is also another group of color-

shifting pigment called all-dielectric thin-film pigments.^{140,141} The optical effects are partially different because of the transparency of these multilayer structures without metal layers. Both color-shifting pigment types, the metal-dielectric as well as the all-dielectric thin-film designs, can be used for several applications and are on the market as so-called optically variable pigments (OVP).¹⁴¹ Such pigments can be applied in automotive paints, plastics, and packaging, mostly as color-shifting optical coatings. A broad application field has been found for prevention of counterfeiting of valued documents such as bank notes, stock certificates, visas, passports, or car licenses.^{141,142} The pigments, when incorporated into security inks and printed onto bank notes and other documents of value, are effective against color copying by printers, copiers, or cameras and unauthorized lithographic reproduction.

VIII. Concluding Remarks

Angle-dependent optical effects are broadly used in industrial products. The effects are achieved using different techniques. Some of them are just at the beginning of their commercialization, such as the liquid crystal applications and the new substrates for oxide layers. Although the optical physics background of thin extended layers is mostly understood, there are hardly any attempts to incorporate the particle characteristics of pigments into the calculations. Also, the coating processes and the constrained sintering of thin oxide layers still wait for a thorough investigation.

IX. List of Abbreviations

- α = relative proportion of pores filled with said material
- δ = phase difference angle
- A_0 = amplitude of incident light
- C_{Chiral} = concentration of the chiral component
- CVD = chemical vapor deposition
- I_0 = intensity of incident light
- I_r = intensity of reflected light

I_t = intensity of transmitted light
 LCP = liquid crystal polymers
 n_0, n_1 = refractive indices
 n_f = refractive index of film
 n_D, n_m = refractive index of bulk
 n_w = refractive index of material filling the pores
 OVP = optically variable pigment
 P = film packing density
 p = helical pitch length
 PVD = physical vapor deposition
 r, r_P, r_S = amplitudes of reflected electromagnetic waves
 r_1, r_2, r_3 = amplitudes of reflected electromagnetic waves from multiple reflections
 R, R_P, R_S = intensities of reflected electromagnetic waves
 R_1, R_2, R_3 = intensities of reflected electromagnetic waves from multiple reflections
 t_1, t_2, t_3 = amplitudes of transmitted electromagnetic waves from multiple reflections
 T_g = glass transition point (of liquid crystals)

X. Acknowledgments

The authors thank Mr. Opfermann and Mr. Plamper for the SEM photos.

XI. References

- (1) (a) Born, M.; Wolf, E. *Principles of Optics: Electromagnetic Theory of Propagation, Interference and Diffraction of Light*, 6th ed.; Cambridge University Press: Cambridge, 1998. (b) Schmidt, C.; Friz, M. *Kontakte (Darmstadt)* 1992, (2), 15.
- (2) (a) Bäumer, W. *Farbe Lack* 1973, 79, 530. (b) Bäumer, W. *Farbe Lack* 1973, 79, 638. (c) Greenstein, L. M. In *Pigment Handbook*; Patton, T. C., Ed.; John Wiley & Sons: New York, 1973; Vol. III, p 357. (d) Iler, R. K. *J. Colloid Interface Sci.* 1966, 21, 569.
- (3) Greenstein, L. M. In *Pigment Handbook*, 2nd ed.; Lewis, P. R., Ed.; John Wiley & Sons: New York, 1988; Vol. I, p 829.
- (4) (a) Smith, S. D. *J. Opt. Soc. Am.* 1958, 48, 43. (b) Epstein, L. I. *J. Opt. Soc. Am.* 1952, 42, 806. (c) Young, L. J. *J. Opt. Soc. Am.* 1961, 51, 967. (d) Baumeister, P. *J. Opt. Soc. Am.* 1958, 48, 955. (e) Dobrowolski, J. A. *Appl. Opt.* 1965, 4, 937. (f) Southwell, W. H. *Appl. Opt.* 1985, 24, 457. (g) Dobrowolski, J. A.; Lowe, D. *Appl. Opt.* 1978, 17, 3039.
- (5) Hofmeister, F. *Eur. Coat. J.* 1990, (3), 80.
- (6) (a) Hofmeister, F.; Pieper, H. *Farbe Lack* 1989, 95, 557. (b) Hofmeister, F. *Farbe Lack* 1987, 93, 799. (c) Emmert, R. *Cosmet. Toiletries* 1989, 104 (7), 57.
- (7) (a) Williamson, S. J.; Cummins, H. Z. *Light and Color in Nature and Art*; Wiley: New York, 1983; p 95. (b) Nassau, K. *The Physics and Chemistry of Color: the Fifteen Causes of Color*; Wiley: New York, 1983.
- (8) (a) Neville, A. C.; Caveney, S. *Biol. Rev.* 1969, 44, 531. (b) Neville, A. C. *Biology of the Arthropod Cuticle*; Springer-Verlag: New York, 1975. (c) Neville, A. C. *Biology of Fibrous Composites: Development beyond the cell membrane*; Cambridge University Press: Cambridge, 1993. (d) Ghiradella, H. *Appl. Opt.* 1991, 30, 3492. (e) Parker, A. R. *Proc. R. Soc. London B* 1998, 265, 967.
- (9) (a) Bernhard, H. *Kontakte (Darmstadt)* 1979, (2), 22. (b) Bernhard, H. *Kontakte (Darmstadt)* 1983, (1), 29. (c) Simon, H. *The Splendor of Iridescence*; Dodd, Mead & Co.: New York, 1971.
- (10) Lee, D. W. *Am. Scientist* 1997, 85, 56.
- (11) Schäffer, T. E.; Ionescu-Zanetti, C.; Proksch, R.; Fritz, M.; Walters, D. A.; Almqvist, N.; Zaremba, C. M.; Belcher, A. M.; Smith, B. L.; Stucky, G. D.; Morse, D. E.; Hansma, P. K. *Chem. Mater.* 1997, 9, 1731.
- (12) (a) Cooper, S. A.; Shetty, R.; Pinsky, J. (Mearl) U.S. Patent 4,310,584, 1982. (b) Wilcox, F. S.; Pinsky, J.; Cooper, S. A. (Mearl) U.S. Patent 4,162,343, 1979.
- (13) Heavens, O. S. *Optical Properties of Thin Solid Films*; Dover Publications: New York, 1965.
- (14) McLeod, H. A. *Thin Films & Optical Filters*; Adam Hilger Ltd.: Bristol, 1986.
- (15) (a) MLC by Leybold Systems GmbH, Wilhelm-Rohn Strasse 25, 63450 Hanau, Germany. (b) TFCalc by Software Spectra, 14025 N.W. Harvest Lane, Portland, OR 97229-3645. (c) Essential Macleod Thin-Film Design Program by Thin Film Center Inc., 2745 E Via Rotonda, Tucson, AZ 85716-5227. (d) Spectrum by Laser Zentrum Hannover e.V., Hollerithallee 8, 30419 Hannover, Germany.
- (16) (a) Bohren, C. F.; Huffman, D. R. *Adsorption and Scattering of Light by Small Particles*; Wiley: New York, 1983; Chapter 11. (b) Kaempf, G. *J. Coat. Technol.* 1979, 51 (655), 51. (c) Benzing, G. *Pigmente und Farbstoffe für die Lackindustrie*, 2nd ed.; Expert Verlag: Ehningen, Germany, 1992; p 120. (d) Buttignol, V. *J. Paint Technol.* 1968, 40, 479. (e) Gunthert, P.; Hauser, P.; Radtke, V. *Rev. Prog. Color.* 1989, 19, 41. (f) Kaempf, G. *Farbe Lack* 1991, 97, 871. (g) Ryde, N. P.; Matijevic, E. *Appl. Opt.* 1994, 33, 7275.
- (17) Atanasov, G.; Thielsch, R.; Popov, D. *Thin Solid Films* 1993, 223, 288.
- (18) (a) Ottermann, C. R.; Bange, K.; Wagner, W.; Laube, M.; Rauch, F. *Sur. Interface Anal.* 1992, 19, 435. (b) Laube, M.; Rauch, F.; Ottermann, C. R.; Anderson O.; Bange, K. *Nucl. Instrum. Methods Phys. Res. B* 1996, 113, 288. (c) Bange, K.; Ottermann, C. R.; Anderson, O.; Jeschowski, U.; Laube, M.; Feile, R. *Thin Solid Films* 1991, 197, 279. (d) Hüppauf, M.; Bange, K.; Lengeler, B. *Thin Solid Films* 1993, 230, 191.
- (19) Thelen, A. In *Ullmann's Encyclopedia of Industrial Chemistry: Thin Films, Section 2.7*, 6th ed. (electronic release); VCH Verlagsgesellschaft: Weinheim, Germany, 1998.
- (20) Macleod, H. A. In *Thin-film Optical Filters*, 2nd ed.; Adam Hilger Ltd.: Bristol, 1986; p 357.
- (21) Martin, P. J.; Netterfield, R. P. *Prog. Opt.* 1986, 13, 113.
- (22) (a) Rogers, D. Z. *Proc. SPIE-Int. Soc. Opt. Eng.* 1989, 1163, 19. (b) Klug, W.; Schneider, R.; Zöller, A. *SPIE 1323 Optical Thin Films III, New Developments* 1990, 88. (c) Segner, J. *Mater. Sci. Eng. A* 1991, 140, 733.
- (23) Schroeder, H. In *Physics of Thin Films*; Hass, G., Thun, R. E., Eds.; Academic Press: New York, 1969; Vol. 5, p 87.
- (24) Kamat, P. V. In *Nanoparticles and Nanostructured Films*; Fendler, J. H., Ed.; Wiley-VCH: Weinheim, Germany, 1998; p 207.
- (25) (a) Schrenk, W.; Wheatley J. *Coextruded Elastomeric Optical Interference Film*; Antec'88, 1988; p 1703. (b) Wilcox, F. S.; Pinsky, S.; Cooper, S. A. (Mearl) U.S. Patent 4,162,343, 1979. (c) Cooper, S. A.; Shetty, R.; Pinsky, J. (Mearl) U.S. Patent 4,310,584, 1982. (d) Shetty, R. S.; Cooper, S. A. (Mearl) U.S. Patent 5,089,318, 1992.
- (26) *Colorimetry*, 2nd ed., CIE Publication 15.2-1986, ISBN 3-900-734-00-3.
- (27) (a) Alfrey, T., Jr.; Gurnee, E. F.; Schrenk, W. J. *Polym. Eng. Sci.* 1969, 9, 400. (b) Schrenk, W. J.; Alfrey, T., Jr. *Pap. Meet.-Am. Chem. Soc., Div. Org. Coat. Plast. Chem.* 1972, 32, 205.
- (28) Shetty, R. S.; Cooper, S. A. (Mearl) European Patent Application 681910, 1995.
- (29) Pfaff, G.; Franz, K.-D.; Emmert, R.; Nitta, K.; Besold, R. In *Ullmann's Encyclopedia of Industrial Chemistry: Pigments, Inorganic, Section 4.3*, 6th ed. (electronic release); VCH Verlagsgesellschaft: Weinheim, Germany, 1998.
- (30) Maisch, R.; Weigand, M. *Pearl Lustre Pigments*; Verlag Moderne Industrie: Landsberg/Lech, Germany, 1991.
- (31) Glausch, R.; Kieser, M.; Maisch, R.; Pfaff, G.; Weitzel, J. *Special Effect Pigments*; Zorll, U., Ed.; Vincentz Verlag: Hannover, Germany, 1998.
- (32) Maisch, R. *Paintindia* (1996 Exhibition Special Issue) 1996, 57.
- (33) (a) Rieger, C. J.; Armanini, L. (Mearl) U.S. Patent 4,134,776, 1979. (b) Franz, K.-D.; Ambrosius, K.; Easelborn, R.; Kieser, M. (Merck KGaA) German Patent 104516, 1984. (c) Watanabe, T.; Nitta, K.; Suzuki, I. (Merck KGaA) European Patent 268918, 1988. (d) Nitta, K.; Suzuki, I. (Merck KGaA) European Patent 342533, 1989.
- (34) (a) Taylor, H. F. *Drugs, Oils, Paints* 1937, 3, 106. (b) Taylor, H. F. *Pearl Essence: Its History, Chemistry and Technology*; Document No. 989, Bureau of Fisheries, U.S. Department of Commerce: 1925; 15.
- (35) Hunsdiecker, H.; Sabetay, S. *Odoriferous Subst. Arom.* 1961, 11, 120.
- (36) Alexander, P. In *Marine Products of Commerce*, 2nd ed.; Tressler, D. K., Lemon, J. McW., Eds.; Reinhold Publ. Corp.: New York, 1951; p 107.
- (37) Alexander, P. *Manuf. Chem.* 1986, 57 (6), 60.
- (38) Bäumer, W. *Farbe Lack* 1979, 79, 530, 638, 747.
- (39) Veitch, J. *Parfum. Kosmet.* 1994, 75, 92.
- (40) Eberts, R. E.; Juby, R. M., II; Venturini, M. T., II (Mearl) European Patent 498686, 1992.
- (41) (a) Wiktorek, S. *Surf. Coat. Aust.* 1987, 24 (5), 11. (b) Funke, W. *Farbe Lack* 1980, 86, 730.
- (42) (a) Franz, G.; Hund, F. (Bayer AG) European Patent 14382, 1980. (b) Ostertag, W.; Bittler, K.; Bock, G. (BASF AG) European Patent 68311, 1983. (c) Uenishi, T.; Harada, H.; Sasaki, K.; Akagi, A.; Yamasaki, T. (Titan Kogyo KK) U.S. Patent 4,373,963, 1983. (d) Ostertag, W. (BASF AG) European Patent 265820, 1988. (e) Ostertag, W. (BASF AG) European Patent 293746, 1987. (f) Ostertag, W.; Schwidetzky, C.; Mronga, N. (BASF AG) European Patent 417567, 1989. (g) Harada, H.; Yamasaki, T.; Sadanaga, E.; Okazaki, T. (Titan Kogyo KK) U.S. Patent 5,500,043, 1996.
- (43) Ostertag, W. *Nachr. Chem. Technol. Lab.* 1994, 42, 849.
- (44) (a) Pfaff, G.; Andes, S. (Merck KGaA) World Patent Application 97/43346, 1997. (b) Pfaff, G.; Andes, S.; Hock, S.; Brenner, R.;

- Brückner, H.-D.; Heyland, A.; Kuntz, M.; Osterried, K.; Schmelz, M. (Merck KGaA) World Patent Application 97/43348, 1997.
- (45) Schröder, H. (Jenaer Glaswerke Schott) U.S. Patent 3,138,475, 1959.
- (46) Haslam, J. H. U.S. Patent 2,941,895, 1960.
- (47) (a) Saegusa, K. (Sumitomo Chemical Co.) European Patent 236952, 1987. (b) Fujita, H.; Saegusa, K. (Sumitomo Chemical Co.) European Patent 240952, 1987.
- (48) Japanese Patent Publication 2528064, 1964.
- (49) Matsushita Electrical Industries, Japanese Patent Application Laid-Open 8812183, 1983.
- (50) (a) Douden, D. K. (Minnesota Mining and Manufacturing) U.S. Patent 4,985,380, 1991. (b) Iida, M.; Sasaki, T.; Watanabe, M. *Chem. Mater.* 1998, 10, 3780.
- (51) (a) Vapaaoksa, P. J.; Eskelinen, P. J. (Kemira Oy) European Patent 377326, 1990. (b) Korpi, T. M.; Hyttinen, S. J. O.; Vapaaoksa, P. J. (Kemira Oy) European Patent Application 325484, 1989. (c) Mattila, H. O.; Eskelinen, P. J. (Kemira Oy) European Patent Application 287354, 1988. (d) DeLuca, C.; Kurtenbach, W. P. (Mearl) U.S. Patent 5,611,851, 1997.
- (52) Ohkura, K.; Matsuzaki, S.; Eskelinen, P. J. (Dainishiseika Color & Chemicals Mfg. Co. Ltd., Kemira Osaka Yhtio) European Patent Application 666292, 1995.
- (53) Pfaff, G.; Hock, S.; Brenner, R.; Brückner, H.-D.; Heyland, A.; Kuntz, M.; Osterried, K.; Andes, S.; Schmelz, M. (Merck KGaA) World Patent Application 97/43347, 1997.
- (54) Bähler, F. (Ciba Specialty Chemicals) European Patent 604370, 1994.
- (55) Bugnon, P.; Herren, F.; Medinger, B. (Ciba-Geigy) European Patent 408498, 1991.
- (56) Bähler, F. (Ciba Specialty Chemicals) European Patent 466649, 1992.
- (57) Löbber, G. In *Ullmann's Encyclopedia of Industrial Chemistry: Phthalocyanines*, 6th ed. (electronic release); VCH Verlagsgesellschaft: Weinheim, Germany, 1998.
- (58) (a) Hashizume, Y.; Kobayashi, S.; Hanibuchi, M. (Toyo Aluminium KK) European Patent Application 747453, 1996. (b) Kameoka, T.; Mizutani, K.; Mori, S.; Watanabe, M. (Sumitomo Sitr Co.) World Patent Application 97/15412, 1997.
- (59) Knox, J. J. W.; Green, W. I. (Silberline Ltd.) European Patent Application 673980, 1995.
- (60) (a) Ostertag, W.; Bittler, K.; Bock, G. (BASF AG) European Patent 33457, 1981. (b) Ostertag, W.; Mronga, N.; Hauser, P. *Farbe Lack* 1987, 93, 973.
- (61) (a) Schmid, R.; Mronga, N. (BASF AG) European Patent 571836, 1993. (b) Schmid, R.; Mronga, N. (BASF AG) European Patent Application 668329, 1995.
- (62) (a) Ostertag, W.; Mronga, N. (BASF AG) U.S. Patent 4,978,394, 1989. (b) Ostertag, W.; Mronga, N. (BASF AG) European Patent 338428, 1989.
- (63) Swallow, B. R. (Mearl) European Patent 401141, 1990.
- (64) Bujard, P.; Bonnard, N. (Ciba Specialty Chemicals) European Patent Application 803549, 1997.
- (65) Atwood, F. C. (Atlantic Research Associates, Inc.) U.S. Patent 2,278,970, 1942.
- (66) (a) Linton, H. R. (Du Pont) U.S. Patent 3,087,828, 1963. (b) Linton, H. R. (Du Pont) U.S. Patent 3,087,829, 1963. (c) Gerasimova, L. G.; Okhrimenko, R. F. *Russ. J. Appl. Chem.* 1997, 70, 1856.
- (67) Quinn, C. A.; Rieger, C. J.; Bolomey, R. A. (Mearl), U.S. Patent 3,437,515, 1969.
- (68) Kohlschütter, H. W.; Rössler, H.; Getrost, H.; Hörl, W.; Reich, W. (Merck KGaA) U.S. Patent 3,553,001, 1971.
- (69) (a) Noguchi, T. *J. Soc. Cosmet. Chem. Jpn.* 1993, 27, 304. (b) Noguchi, T.; Sakamoto, I. *Shikizai Kyokaishi* 1997, 70, 359; *Chem. Abstr.* 1997, 127, 127, 137099.
- (70) (a) Bernhard, H.; Esselborn, R. (Merck KGaA) U.S. Patent 4,076,551, 1976. (b) Rau, A.; Franz, K.-D. (Merck KGaA) U.S. Patent 4,545,821, 1985. (c) Armanini, L.; Johnson, C. E. (Mearl) U.S. Patent 4,047,969, 1977.
- (71) (a) Eberts, R. E. (Mearl) U.S. Patent 3,980,491, 1976. (b) Rands, R. D.; Chapman, D. W. (Mallinckrodt) U.S. Patent 3,597,250, 1971.
- (72) Reynders, P.; Brückner, H.-D. (Merck KGaA) European Patent 544867, 1993.
- (73) Prengel, C.; Reynders, P.; Hohenberger, S. (Merck KGaA) U.S. Patent 5,356,471, 1993.
- (74) Franz, K.-D.; Ambrosius, K.; Prengel, C. (Merck KGaA) European Patent 354374, 1989.
- (75) Schmid, R.; Mronga, N.; Ochmann, H.; Schwidetzky, C. (BASF AG) European Patent 632110, 1995.
- (76) Bolomey, R. A. (Mearl) German Patent 1467466, 1968.
- (77) Yamamoto, M.; Ando, A.; Kosugi, T. (Topy Industries Ltd.) European Patent Application 723 997, 1996.
- (78) Brückner, H.-D.; Schmidt, C.; Seibel, C.; Heyland, A.; Schank, C. (Merck KGaA) German Patent Application 19618569, 1998.
- (79) Dietz, J.; Parusel, M.; Schilling, M.; Ambrosius, K. (Merck KGaA) German Patent Application 19638708, 1998.
- (80) Kumar, K. N. P.; Keizer, K.; Burggraaf, A.; Okubo, T.; Nagamoto, H. J. *J. Mater. Chem.* 1993, 3, 1151.
- (81) Eskelinen, P. *J. Solid State Chem.* 1992, 100, 356.
- (82) Eskelinen, P.; Ritala, M.; Leskela, M. *J. Solid State Chem.* 1993, 103, 160.
- (83) Eskelinen, P. *Thermochim. Acta* 1993, 214, 19.
- (84) Eskelinen, P. *J. Solid State Chem.* 1993, 106, 213.
- (85) Eskelinen, P. *Polymers Paint Colour J.* 1995, S4.
- (86) Hildenbrand, V. D.; Doyle, S.; Fuess, H.; Pfaff, G.; Reynders, P. *Thin Solid Films* 1997, 304, 204.
- (87) Jinsheng, L.; Junru, T.; Yihuan, S.; Jinling, Z.; Xiuzeng, C. *Trans. Tianjin Univ.* 1995, 1, 26.
- (88) Esselborn, R.; Bernhard, H. (Merck KGaA) German Patent 2522572, 1976.
- (89) (a) Ambrosius, K.; Knapp, A.; Plamper, H.; Esselborn, R. (Merck KGaA) European Patent 271767, 1988. (b) DeLuca, C. V.; Miller, H. A.; Waitkins, G. R. (Mearl) U.S. Patent 4,038,099, 1971.
- (90) Kumar, K. N. P.; Keizer, K.; Burggraaf, A. *J. Mater. Sci. Lett.* 1994, 13, 59.
- (91) DeLuca, C. V., Jr. (Mearl) U.S. Patent 5,433,779, 1994.
- (92) Kimura, A.; Suzuki, F. (Shiseido) German Patent 3433657, 1985.
- (93) (a) Franz, K.-D.; Ambrosius, K.; Wilhelm, S.; Nitta, K. (Merck KGaA) European Patent 632821, 1993. (b) Shio, S.; Suzuki, F. (Shiseido) European Patent 601761, 1994. (c) Ostertag, W.; Mronga, N.; Graessle, U. (BASF AG) European Patent 332071, 1989.
- (94) (a) Prengel, C.; Bernhard, K. (Merck KGaA) U.S. Patent 5,322,561, 1994. (b) Kuntz, M.; Gross, M.; Zschau, S.; Pfaff, G.; Bernhard, K.; Vogt, R. (Merck KGaA) U.S. Patent 5,753,024, 1998. (c) Bernhard, K.; Pfaff, G.; Vogt, R. (Merck KGaA) European Application 675175, 1995.
- (95) Ito, H.; Handa, J.; Takagi, Y.; Minohara, T. (Toyota Jidosha Kabushiki Kaisha) European Patent 351932, 1990.
- (96) (a) Marshall, W. J. (Du Pont) U.S. Patent 3,440,075, 1969. (b) Handa, J.; Ito, H.; Monohara, T.; Takagi, Y. (Toyota Jidosha Kabushiki Kaisha) European Patent 360513, 1990.
- (97) Kimura, A.; Ikuta, Y. (Shiseido Co. Ltd.) European Patent Application 761773, 1997.
- (98) Minohara, T.; Ito, H.; Handa, J.; Tanaka, Y. (Toyota Jidosha Kabushiki Kaisha) European Patent 450945, 1991.
- (99) (a) Armanini, L. (Mearl) U.S. Patent 4,146,403, 1979. (b) Bernhard, H.; Esselborn, R.; Hesse, R.; Russmann, R. (Merck KGaA) U.S. Patent 3,926,659, 1975.
- (100) (a) Franz, K.-D.; Ambrosius, K. (Merck KGaA) European Patent 211351, 1987. (b) Emmert, R.; Weigand, M. (Merck KGaA) European Patent 307747, 1989.
- (101) Franz, K.-D.; Ambrosius, K.; Knapp, A.; Brückner, H.-D. (Merck KGaA), European Patent 246523, 1987.
- (102) (a) Schmidt, C.; Bauer, G.; Osterried, K.; Uhlig, M.; Schul, N.; Brenner, R.; Vogt, R. (Merck KGaA) World Patent 93/08237, 1993. (b) Teaney, S.; Pfaff, G.; Nitta, K. *Eur. Coat. J.* 1999, (4), 90.
- (103) Venturini, M. T.; LaVallee, C.; Cacace, D. (Engelhard Co.) World Patent Application 97/46624, 1997.
- (104) Nitta, K.; Shau, T. M.; Sugahara, J. (Merck KGaA) European Patent Application 763573, 1997.
- (105) Ohtsu, K.; Sato, N. (Sakai Kagaku Kogyo KK) World Patent Application 97/40118, 1997.
- (106) (a) Saida, K.; Saegusa, K. (Sumitomo Chemical Co.) Japanese Patent Application Sho60-126718, 1986. (b) Pfaff, G.; Andes, S.; Bauer, G.; Brenner, R.; Brückner, H.-D.; Heyland, A.; Kuntz, M.; Osterried, K.; Schmelz, M. (Merck KGaA) World Patent Application 97/02650, 1997.
- (107) Pfaff, G. (Merck KGaA) German Patent Application 19618566, 1997.
- (108) Souma, T.; Ishidoya, M.; Nakamichi, T.; Takai, N. (Nippon Oil and Fats Co.) European Patent 328906, 1989.
- (109) Nadkarny, S. K. (Alcan International Ltd.) World Patent Application 95/14732, 1995.
- (110) (a) Uchiyama, T.; Hasegawa, M.; Ootsuka, T.; Matsumoto, H. (Showa Aluminum KK) U.S. Patent 4,158,074, 1979. (b) Reisser, W. (Eckart-Werke) World Patent Application 96/38505, 1996.
- (111) Makow, D. *Color Res. Appl.* 1986, 11, 205.
- (112) Makow, D. *Mol. Cryst. Liq. Cryst.* 1985, 123, 347.
- (113) (a) De Gennes, P. G. *The Physics of Liquid Crystals*; Clarendon Press: Oxford, 1974. (b) Sage, I. In *Ullmann's Encyclopedia of Industrial Chemistry: Liquid Crystals*, 6th ed. (electronic release); VCH Verlagsgesellschaft: Weinheim, Germany, 1998. (d) Gray, D. *Thermotropic Liquid Crystals*; Wiley: New York, 1987. (e) Ballauff, M. *Chem. Unserer Zeit* 1988, 22, 63.
- (114) Robble, M.; Brett, M. J.; Lakhtakia, J. *Nature* 1996, 384, 616.
- (115) Tamaoki, N.; Parfenov, A. V.; Masaki, A.; Matsuda, H. *Mater. Res. Soc. Symp. Proc.* 1998, 488, 915.
- (116) Kreuzer, F. H.; Maurer, R.; Stohrer, J. *Mater. Res. Soc. Symp. Proc.* 1996, 425, 3.
- (117) Krücke, B.; Schlossarek, M.; Zschke, H. *Acta Polym.* 1988, 39, 607.

- (118) Kreuzer, F.-H.; Gawhary, M. E.; Winkler, R.; Finkelmann, H. (Consortium für elektrochemische Industrie) European Patent 60335, 1981.
- (119) Richards, R. D. C.; Hawthorne, W. D.; Hill, J. S.; White, M. S.; Lacey, D.; Semlyen, J. A.; Gray, G. W.; Kendrick, T. C., *J. Chem. Soc., Chem. Commun.* 1990, 95.
- (120) Kreuzer, F. H.; Maurer, R.; Spes, P. *Makromol. Chem. Makromol. Symp.* 1991, 50, 215.
- (121) Kreuzer, F. H.; Andrejewski, D.; Haas, W.; Häberle, N.; Riepl, G.; Spes, P. *Mol. Cryst. Liq. Cryst.* 1991, 199, 345.
- (122) Andrejewski, D.; Gohary, M.; Luckas, H.-J.; Winkler, R.; Kreuzer, F.-H. (Consortium für elektrochemische Industrie) European Patent 358208, 1989.
- (123) Finkelmann, H.; Rehage, G.; Kreuzer, F. H. (Consortium für elektrochemische Industrie) European Patent 66137, 1985.
- (124) Maurer, R.; Andrejewski, D.; Kreuzer, F. H.; Müller, A. *SID Int. Symp. Dig. Technol. Pap.* 1990, 21, 110.
- (125) Häberle, N.; Leigeber, H.; Maurer, R.; Miller, A.; Stohrer, J.; Buchecker, R.; Fünfschilling, J.; Schadt, M. *SID Int. Display Res. Conf. San Diego* 1991, 57.
- (126) Pinsl, J.; Bräuchle, C.; Kreuzer, F. H. *J. Mol. Electron.* 1987, 3, 9.
- (127) Müller-Rees, C.; Maurer, R.; Stohrer, J.; Kreuzer, F.-H.; Jung, S.; Csellich, F. (Consortium für elektrochemische Industrie) European Patent 601483, 1992.
- (128) Korenic, E. M.; Jacobs, S. D.; Faris, S. M.; Li, L. *Proc. IS&T/SID* 1995, 60.
- (129) Eberle, H. J.; Miller, A.; Kreuzer, F. H. *Liq. Cryst.* 1989, 5, 907.
- (130) George, N.; Stone, T. In *Ullmann's Encyclopedia of Industrial Chemistry: Holography*, 6th ed. (electronic release); VCH Verlagsgesellschaft: Weinheim, Germany, 1998.
- (131) (a) Bartolini, R.; Hannan, W.; Karlsons, D.; Lurie, M. *Appl. Opt.* 1970, 9, 2283. (b) Iwata, F.; Tsujinchi, J. *Appl. Opt.* 1974, 13, 1327. (c) Cowan, J.; Slafer, W. D. *Proc. Soc. Photo-Opt. Instrum. Eng.* 1985, 600, 49. (d) Burns, J. R. *Proc. Soc. Photo-Opt. Instrum. Eng.* 1985, 523, 7.
- (132) (a) Caulfield, H. J. In *Handbook of Optical Holography*; Academic Press: New York, 1979. (b) Hariharan, P. In *Optical Holography*; Cambridge University Press: Cambridge, 1987. (c) Beiser, L. In *Holographic Scanning*; Wiley: New York, 1988.
- (133) Meikka, R. G.; Benoit, D. R.; Thomas, R. M.; Rettker, J. P.; Josephy, K. (Avery Dennison Corp.) World Patent Application 93/23481, 1993.
- (134) Stone, T.; George, N. *Appl. Opt.* 1985, 24, 3797.
- (135) Totsuya Co., Ltd., Japanese Patent JP 4,219,610, 1992.
- (136) (a) King, J. G.; Mackara, S. R.; Mickish, D. J.; Spooner, D. L. (E. I. Du Pont de Nemours and Co.) U.S. Patent 5,415,950, 1993. (b) King, J. G.; Mackara, S. R.; Mickish, D. J.; Spooner, D. L. (E. I. Du Pont de Nemours and Co.) U.S. Patent 5,500,310, 1994. (c) King, J. G.; Mackara, S. R.; Mickish, D. J.; Spooner, D. L. (E. I. Du Pont de Nemours and Co.) U.S. Patent 5,500,311, 1994. (d) King, J. G.; Mackara, S. R.; Mickish, D. J.; Spooner, D. L. (E. I. Du Pont de Nemours and Comput.) U.S. Patent 5,500,313, 1994.
- (137) Berning, P. H.; Phillips, R. W. (Optical Coating Laboratory, Inc.) U.S. Patent 4,705,356, 1984.
- (138) Ash, G. S. (Optical Coating Laboratory, Inc.) U.S. Patent 4,434,010, 1981.
- (139) Berning, P. H.; Phillips, R. W. (Flex Products, Inc.) U.S. Patent 4,930,866, 1988.
- (140) (a) Hadley, L. N.; Dennison, D. M. *J. Opt. Soc. Am.* 1947, 37, 483. (b) Turner, A. F. *J. Phys. Rad.* 1950, 11, 444.
- (141) Phillips, R. W.; Bleikolm, A. F. *Appl. Opt.* 1996, 35, 5529.
- (142) Dobrowolski, J. A.; Baird, K. M.; Carman, P. D.; Waldorf, A. *Opt. Acta* 1973, 20, 925.

CR970075U



US 20020104461A1

(19) **United States**(12) **Patent Application Publication** (10) **Pub. No.: US 2002/0104461 A1**
Schmidt et al. (43) **Pub. Date: Aug. 8, 2002**(54) **SILVER-COLORED LUSTER PIGMENT**(30) **Foreign Application Priority Data**(75) **Inventors: Christoph Schmidt, Kriftel (DE);
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Dec. 7, 2000 (DE)..... 100 61 178.8

Publication Classification(51) **Int. Cl.⁷ C04B 14/20; C04B 14/00**(52) **U.S. Cl. 106/417**

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chränkter Haftung, Darmstadt (DE)**(21) **Appl. No.: 10/003,118**(22) **Filed: Dec. 6, 2001**

The present invention relates to silver-colored luster pigments based on multiply coated platelet-shaped substrates, which has at least one layer sequence of TiO₂, a colorless coating and another TiO₂ layer. The pigment can optionally have an outer protective layer. These luster pigments are useful and to the use thereof in paints, coatings, printing inks, including security printing inks, plastics, ceramic materials, glasses, cosmetic formulations and for producing pigment preparations and dry product forms such as granules, chips, pellets and briquettes.

SILVER-COLORED LUSTER PIGMENT

[0001] The present invention relates to silver-colored luster pigments based on multiply coated platelet-shaped substrates.

[0002] Luster or effect pigments are widely used in industry, especially in automotive coatings, decorative coatings, plastic, paints, printing inks and cosmetic formulations.

[0003] Luster pigments with an angle-dependent color change between a number of interference colors exhibit a color interplay which makes them particularly useful for automotive coatings and anti-counterfeit applications.

[0004] The prior art discloses processes for preparing pearl luster pigments whereby alternating layers of high and low refractive index can be applied to finely divided substrates. Such pigments based on multiply coated platelet-shaped substrates are known for example from U.S. Pat. No. 4,434,010, JP H7-759, U.S. Pat. No. 3,438,796, U.S. Pat. No. 5,135,812, DE 44 05 494, DE 44 37 753, DE 195 16 181 and DE 195 15 988.

[0005] Of particular importance in this context are mineral-based pearl luster pigments. Pearl luster pigments are prepared by coating an inorganic platelet-shaped support with a high refractive, usually oxidic layer. The color of these pigments is caused by wavelength-selective partial reflection and interference of the reflected or transmitted light at the medium/oxide or oxide/substrate boundaries.

[0006] The interference color of these pigments is determined by the thickness of the oxide layer. The hue of an interference silver pigment is created by a single (in the optical sense) high refractive layer whose optical thickness gives rise to a reflection maximum (1st order) at about 500 nm in the visible wavelength range. The wavelength of about 500 nm is perceived by the human eye as the color green. However, the intensity curve of this maximum along its wavelength axis is so broad that so much light is reflected in the entire visible-light region that what the human eye sees is very bright but colorless.

[0007] One familiar with the optics of thin layers, particularly with the coating of optical components, would predict that the intensity at the interference maximum would increase by about 60% compared with the monolayer system. The profile of the light reflected by interference would accordingly become significantly more pronounced, so that such a multilayered system would be expected to have a green reflection color.

[0008] It has now been found that, surprisingly, an actual interference system in the form of alternating high refractive layers of TiO_2 and low refractive layers on a transparent substrate platelet is perceived not as green but as silvery at certain layer thicknesses.

[0009] The present invention accordingly provides silver-colored luster pigments based on multiply coated platelet-shaped substrates, comprising at least one layer sequence of

[0010] (A) a high refractive coating consisting of TiO_2 and having a thickness of 5-200 nm,

[0011] (B) a colorless coating having a refractive index $n < 1.8$ and a thickness of 10-300 nm,

[0012] (C) a high refractive coating consisting of TiO_2 and having a thickness of 5-200 nm, and optionally

[0013] (D) an outer, protective layer.

[0014] The silver pigments according to the invention are superior to existing pearl luster pigments in the silver region because of

[0015] a stronger, particularly metallic luster at steep viewing angles

[0016] a higher transparency at flat viewing angles and

[0017] a lighter masstone color.

[0018] The invention further provides for the use of the silver pigments according to the invention in paints, coatings, plastics, ceramic materials, glasses, cosmetic formulations, and especially in printing inks. The pigments according to the invention are also useful for preparing pigment formulations and also for preparing dry product forms, for example granules, chips, pellets, briquettes, etc. The dry product forms are useful for printing inks in particular.

[0019] Useful base substrates for the multilayer pigments according to the invention are selectively or nonselectively absorbing platelet-shaped substrates. Preferred substrates are sheet-silicates. Particularly useful are natural and/or synthetic mica, talc, kaolin, platelet-shaped iron or aluminium oxides, glass platelets, SiO_2 platelets, Al_2O_3 platelets, TiO_2 platelets, graphite platelets, synthetic support-free platelets, titanium nitride, titanium silicide, liquid crystal polymers (LCPs), holographic pigments, BiOCl , platelet-shaped mixed oxides, for example FeTiO_3 , Fe_2TiO_5 , or other comparable materials.

[0020] The size of the base substrates is not critical per se and can be adapted to the particular end use. In general, the platelet-shaped substrates are between 0.005 and 10 μm , preferably between 0.05 and 5 μm , in thickness. In the other two dimensions; i.e., in length and in width, the platelet-shaped substrates extend, independently in each of said other two dimensions, from 1 to 500 μm , preferably from 2 to 200 μm , and more preferably from 5 to 60 μm .

[0021] The thickness on the base substrate of the individual layers (A), (B) and (C) having a high refractive index or a low refractive index is important for the optical properties of the pigment. To obtain the silver pigment with an intensive luster effect, the thicknesses of the individual layers have to be precisely adjusted with respect to one another.

[0022] The thickness of the layer (A) or (C) is 5-200 nm, preferably 10-100 nm, and more preferably 20-70 nm. The TiO_2 layers (A) and (C) can have identical or different thicknesses. The thickness of layer (B) is 10-300 nm, preferably 20-100 nm, and more preferably 30-80 nm.

[0023] The pigments can contain a plurality of identical or different combinations of layer packets, but it is preferable to coat the substrate with only one layer packet (A)+(B)+(C)+ optionally (D). To intensify the color strength, the pigment according to the invention can contain up to 4 layer packets, i.e., 1, 2, 3 or 4 packets. Layer sequences (A)+(B)+(C)+(B)+(C), (A)+(B)+(C)+(B)+(C)+(B)+(C) and (A)+(B)+(C)+(B)+(C)+(B)+(C)+(B)+(C) are possible. In this situa-

tion the thickness of all the layers on the substrate should preferably not exceed 3 μm . It is preferable to apply an odd number of layers to the platelet-shaped substrate with a high refractive layer both as the innermost and outermost layer. Preference is given to a construction of three optical interference layers in the sequence (A) (B) (C).

[0024] Colorless low refractive index materials useful as the coating (B) are preferably metal oxides or those corresponding oxyhydrates, for example SiO_2 , Al_2O_3 , $\text{AlO}(\text{OH})$, B_2O_3 , MgF_2 , MgSiO_3 or a mixture thereof. Layer (B) is preferably an SiO_2 layer.

[0025] The pigments according to the invention are easy to produce by generating a plurality of high and low refractive index interference layers having a precisely defined thickness and a smooth surface on the finely divided platelet-shaped substrates.

[0026] The metal oxide layers are preferably applied wet chemically, for example by using the wet-chemical coating processes developed for producing pearl luster pigments. Such processes are described for example in DE 14 67 468, DE 19 59 988, DE 20 09 566, DE 22 14 545, DE 22 15 191, DE 22 44 298, DE 23 13 331, DE 25 22 572, DE 31 37 808, DE 31 37 809, DE 31 51 343, DE 31 51 354, DE 31 51 355, DE 32 11 602, DE 32 35 017 or else in further patent documents and other publications known to one skilled in the art.

[0027] The substrate particles in a wet coating are suspended in water and admixed with one or more hydrolysable metal salts or a silicate solution at a suitable hydrolysis pH, chosen so that the metal oxides or oxyhydrates are directly precipitated onto the platelets without coprecipitations. The pH is customarily kept constant by simultaneous metered addition of a base and/or acid. The pigments are then separated off, washed and dried at 50-150° C. for 6-18 h and optionally calcined for 0.5-3 h, in which case the calcination temperature can be optimized with regard to the particular coating present. In general, the calcination temperatures are between 250 and 1000° C., preferably between 350 and 900° C. If desired, the pigments can be separated off, dried and optionally calcined after application of individual coatings and then resuspended to precipitate further layers.

[0028] Furthermore, the coating may also be effected in a fluidized bed reactor by gas phase coating, in which case, for example, the processes proposed in EP 0 045 851 and EP 0 106 235 for producing pearl luster pigments can be employed with appropriate changes.

[0029] The hue of the pigments can be varied within very wide limits, subject to the silver effect obtained, by varying the coating rates and the resulting layer thicknesses. Beyond purely quantitative means, the fine adjustment for certain hues can be achieved by approaching the desired color under visual or instrumental control.

[0030] To increase light, water and weather stability, it is frequently advisable, depending on the field of use, to subject the ready-produced pigment to an aftercoating or aftertreatment. Useful aftercoatings or aftertreatments include for example the processes described in DE-C 22 15 191, DE-A 31 51 354, DE-A 32 35 017 or DE-A 33 34 598. The aftercoating layer (D) further enhances the chemical stability and/or facilitates the handling of the pigment, especially its incorporation into various media.

[0031] The pigments according to the invention are compatible with a multiplicity of color systems, preferably in the field of coatings, paints and printing inks. To produce printing inks, for example for intaglio printing, flexographic printing, offset printing, offset overprint coating, there are a multiplicity of suitable binders, especially water-soluble grades as sold for example by the companies BASF, Marabu, Pröll, Sericol, Hartmann, Gebr. Schmidt, Sicpa, Aarberg, Sieberg, GSB-Wahl, Follmann, Ruco or Coates Screen INKS GmbH. The printing inks can be waterborne or solventborne. Furthermore, the pigments are also useful for the laser marking of paper and plastics and also for applications in the agricultural sector, for example, for greenhouse film, and also for the coloring of tarpaulins.

[0032] Since the silver pigments according to the invention combine superior luster with high transparency and a neutral masstone color, they can be used for obtaining particularly potent effects in various application media, for example, in cosmetic formulations, nail varnishes, lipsticks, compact powders, gels, lotions, soaps, toothpaste, coatings, automotive coatings, industrial coatings, powder coatings, in plastics, ceramics and, in the hobby sector, for window colors.

[0033] It should be readily understood that for various end uses, the multilayer pigments may also be used with advantage in blends with organic dyes, organic pigments or other pigments, for example transparent, hiding white, color and black pigments and also with platelet-shaped iron oxides, organic pigments, holographic pigments, LCPs (liquid crystal polymers), and conventional transparent, colored and black luster pigments based on metal oxide coated mica and SiO_2 platelets etc. The multilayer pigments can be blended with commercially available pigments and fillers in any proportion.

[0034] The pigments according to the invention are further useful for producing flowable pigment preparations and dry product forms, especially for printing inks, comprising one or more pigments according to the invention, binders and optionally one or more additives.

[0035] Suitable binders are those which are commonly added to paints and varnishes and are listed, for example, in Karsten, Lackrohstofftabellen, 8th edition, 1987. Suitable binders are of those binders or binder mixtures that are customarily used for printing inks, examples being those based on cellulose, polyacrylate, polymethacrylate, alkyd, polyester, polyphenol, urea, melamine, polyterpene, polyvinyl, polyvinyl chloride and polyvinylpyrrolidone resins, polystyrenes, polyolefins, indene-coumarone, hydrocarbon, ketone, aldehyde and aromatic-formaldehyde resins, carbamic acid resins, sulfonamide resins and epoxy resins, polyurethanes and/or natural oils or derivatives of the substances mentioned.

[0036] Additives, for example, are pH regulators, defoamers, wetting agents, anti-settling agents, levelling agents, siccatives and thixotropic agents. These are auxiliaries customary in the coatings industry.

[0037] The invention thus also provides for the use of the pigments in formulations such as paints, printing inks, including security printing inks, coatings, plastics, ceramic materials, glasses and cosmetic formulations.

[0038] The examples hereinbelow will now describe the invention more particularly without, however, limiting it.

[0039] Without further elaboration, it is believed that one skilled in the art can, using the preceding description, utilize the present invention to its fullest extent. The following preferred specific embodiments are, therefore, to be construed as merely illustrative, and not limitative of the remainder of the disclosure in any way whatsoever.

[0040] In the foregoing and in the following examples, all temperatures are set forth uncorrected in degrees Celsius; and, unless otherwise indicated, all parts and percentages are by weight.

[0041] The entire disclosure of all applications, patents and publications, cited above or below, and of corresponding German application No. 10061178.8, filed Dec. 7, 2000, is hereby incorporated by reference.

EXAMPLES

Example 1

[0042] 100 g of mica of particle size 10-60 μm in 2 l of demineralized water is heated to 75° C. On attainment of this temperature, a solution of 3 g of $\text{SnCl}_4 \times 5 \text{ H}_2\text{O}$ in 90 g of water is gradually added to the mica suspension while stirring. The pH is kept constant at 2.0 using 32% aqueous sodium hydroxide solution. The pH is then lowered to 1.8 and at this pH 270 g of 32% TiCl_4 solution is added in while the pH is kept constant using 32% aqueous sodium hydroxide solution. The pH is then raised to 7.5 and at this pH 270 g of sodium silicate solution (13.5% by weight of SiO_2) is gradually added in while the pH is kept constant at 7.5 using 10% HCl. Next, 300 g of 32% TiCl_4 solution is added at pH 1.8. After 0.5 h of stirring at pH 1.8, the coated mica pigment is filtered off, washed and dried at 110° C. for 16 h. Finally, the pigment is calcined at 800° C. for 1 h.

Example 2

[0043] 100 g of mica of particle size 10-60 μm in 2 l of demineralized water is heated to 75° C. On attainment of this temperature, a solution of 3 g of $\text{SnCl}_4 \times 5 \text{ H}_2\text{O}$ in 90 g of water is gradually added to the mica suspension with vigorous stirring. The pH is kept constant at 2.0 using 32% aqueous sodium hydroxide solution. The pH is then lowered to 1.8 and at this pH 380 g of 32% TiCl_4 solution is added in while the pH is kept constant using 32% aqueous sodium hydroxide solution. The pH is then raised to 7.5 and at this pH 380 g of sodium silicate solution (13.5% by weight of SiO_2) is gradually added in while the pH is kept constant at 7.5 using 10% HCl. Next, 380 g of 32% TiCl_4 solution is added at pH 1.8. After 0.5 h of stirring at pH 1.8, the coated mica pigment is filtered off, washed and dried at 110° C. for 16 h. Finally, the pigment is calcined at 800° C. for 1 h.

Example 3

[0044] 100 g of mica of particle size 10-60 μm in 2 l of demineralized water is heated to 75° C. On attainment of this temperature, a solution of 3 g of $\text{SnCl}_4 \times 5 \text{ H}_2\text{O}$ in 90 g of water is gradually added to the mica suspension with vigorous stirring. The pH is kept constant at 2.0 using 32% aqueous sodium hydroxide solution. The pH is then lowered to 1.8 and at this pH 220 g of 32% TiCl_4 solution is added in while the pH is kept constant using 32% aqueous sodium

hydroxide solution. The pH is then raised to 7.5 and at this pH 215 g of sodium silicate solution (13.5% by weight of SiO_2) is gradually added in while the pH is kept constant at 7.5 using 10% HCl. Next, 300 g of 32% TiCl_4 solution is added at pH 1.8. After 2.5 h of stirring at pH 1.8, the coated mica pigment is filtered off, washed and dried at 110° C. for 16 h. Finally, the pigment is calcined at 800° C. for 1 h.

Example 4

[0045] 100 g of mica of particle size 10-60 μm in 2 l of demineralized water is heated to 75° C. On attainment of this temperature, a solution of 330 g of 32% TiCl_4 solution is added in while the pH is kept constant using 32% aqueous sodium hydroxide solution. The pH is then raised to 7.5 and at this pH 270 g of sodium silicate solution (13.5% by weight of SiO_2) is gradually added in while the pH is kept constant at 7.5 using 10% HCl. Next, 250 g of 32% TiCl_4 solution is added at pH 2.2. After 5 h of stirring at pH 2.2, the coated mica pigment is filtered off, washed and dried at 110° C. for 16 h. Finally, the silver pigment is calcined at 800° C. for 1 h.

[0046] The following table shows the calorimetric data of the pigments according to the invention in comparison with a silver pigment representing the prior art (Phyma-Lab values measured against black background with gloss 22.5°/22.5°):

Pigment	L	a	b	C	Gloss number	Hiding power
Silver-colored pearl luster pigment Iridion® 103 (TiO_2 mica pigment of particle size 10-60 μm from Merck KGaA)	83.6	-1.4	-1.9	2.4	58.5	30.6
Silver pigment of Example 1	90.2	-8.1	-11.4	14.0	60.9	33.6
Silver pigment of Example 2	93.0	-5.5	13.0	14.1	61.3	37.0
Silver pigment of Example 3	79.2	-10.3	-23.3	25.5	59.8	25.4
Interference pigment of Example 4	84.5	-8.1	-10.5	13.3	61.4	27.2

[0047] The preceding examples can be repeated with similar success by substituting the generically or specifically described reactants and/or operating conditions of this invention for those used in the preceding examples.

[0048] From the foregoing description, one skilled in the art can easily ascertain the essential characteristics of this invention and, without departing from the spirit and scope thereof, can make various changes and modifications of the invention to adapt it to various usages and conditions.

1. A silver-colored luster pigment comprising a multiply coated platelet-shaped substrate and at least one layer sequence of

layer (A) a high refractive coating consisting of TiO_2 which has a thickness of 5-200 nm,

layer (B) a colorless coating having a refractive index $n \leq 1.8$ and a thickness of 10-300 nm, and

layer (C) a high refractive coating consisting of TiO_2 which has a thickness of 5-200 nm, and optionally

layer (D) an outer, protective layer.

2. A luster pigment according to claim 1, wherein the platelet-shaped substrate is a sheet silicate.

3. A luster pigment according to claim 1, wherein the platelet-shaped substrate is a natural mica, a synthetic mica, talc, kaolin, a platelet-shaped iron oxide, a platelet-shaped aluminum oxide, a glass platelet, SiO_2 platelets, TiO_2 platelets, Al_2O_3 platelets, a graphite platelet, a synthetic support-free platelet, titanium nitride, titanium silicide, a liquid crystal polymer, a holographic pigment, BiOCl , platelet-shaped mixed oxides of FeTiO_3 or FeTiO_5 .

4. A luster pigment according to claim 1, wherein layer (B) comprises silicon dioxide, aluminum oxide, $\text{AlO}(\text{OH})$, B_2O_3 , MgSiO_3 , magnesium fluoride or mixtures thereof.

5. A luster pigment according to claim 1, wherein layer (B) comprises silicon dioxide.

6. A luster pigment according to claim 1, comprising a layer sequence of (A)+(B)+(C)+(B)+(C).

7. A luster pigment according to claim 1, comprising a layer sequence of (A)+(B)+(C)+(B)+(C)+(B)+(C).

8. A luster pigment according to claim 1, comprising a layer sequence of (A)+(B)+(C)+(B)+(C)+(B)+(C)+(B)+(C).

9. A luster pigment according to claim 1, wherein the platelet-shaped substrates are 0.005 to 10 μm in thickness, and 1 to 500 μm in length.

10. A luster pigment according to claim 9, wherein the platelet-shaped substrates are 0.5 to 5 μm in thickness, and independently of the thickness, 2 to 200 μm in length.

11. A luster pigment according to claim 9, wherein the platelet-shaped substrates are 5 to 60 μm in length.

12. A luster pigment according to claim 1, wherein layers (A) and (C) each independently of one another are 10 to 100 nm thick.

13. A luster pigment according to claim 1, wherein layers (A) and (C) each independently of one another are 20 to 70 nm thick.

14. A luster pigment according to claim 1, wherein layer (B) is 20 to 100 nm thick.

15. A luster pigment according to claim 1, wherein layer (B) is 30 to 80 nm thick.

16. A luster pigment according to claim 1, wherein the total thickness of all the layers on the substrate is at most 3 μm .

17. A luster pigment according to claim 8, wherein the total thickness of all the layers on the substrate is at most 3 μm .

18. A process for preparing a luster pigment of claim 1, wherein a substrate is coated wet chemically by hydrolytic decomposition of metal salts in an aqueous medium, or is gas phase coated in a fluidized bed reactor.

19. A method of coloring a paint, a coating, a painting ink, a security printing ink, a plastic, a ceramic material, glasses, a cosmetic formulation, a nail varnish, a lipstick, a compact powder, a gel, a lotion, a soap, a toothpaste, an automotive coating, an industrial coating, a powder coating, or a window by adding or applying a luster pigment of claim 1.

20. A pigment preparation comprising at least one luster pigment according to claim 1, at least one binder, and optionally at least one additive.

21. A pigment preparation according to claim 20 further comprising an organic dye, another pigment than a pigment according to claim 1, a liquid crystal polymer, a platelet-shaped iron oxide, a filler or mixtures thereof.

22. A paint, a coating, a painting ink, a security printing ink, a plastic, a ceramic material, glasses, a cosmetic formulation, a nail varnish, a lipstick, a compact powder, a gel, a lotion, a soap, a toothpaste, an automotive coating, an industrial coating, a powder coating, or a window colored by the method according to claim 18, in the form of granules, chips, pellets and/or briquettes.

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